CONSEQUENCE ANALYSIS OF AQUEOUS AMMONIA SPILLS USING AN IMPROVED LIQUID POOL EVAPORATION MODEL

A Thesis

by

VIJAY RAGHUNATHAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2004

Major Subject: Chemical Engineering

CONSEQUENCE ANALYSIS OF AQUEOUS AMMONIA SPILLS USING AN IMPROVED LIQUID POOL EVAPORATION MODEL

A Thesis

by

VIJAY RAGHUNATHAN

Submitted to Texas A&M University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Approved as to style and content by:

M. Sam Mannan (Chair of Committee)	Mahmoud El-Halwagi (Member)
Kenneth Hall (Head of Department)	Michael K. Lindell (Member)

December 2004

Major Subject: Chemical Engineering

ABSTRACT

Consequence Analysis of Aqueous Ammonia Spills Using an Improved Liquid Pool Evaporation Model. (December 2004)

Vijay Raghunathan, B.Tech, University of Madras

Chair of Advisory Committee: Dr. Sam Mannan

Source term modeling is the key feature in predicting the consequences of releases from hazardous fluids. Aqueous ammonia serves the purpose of a reducing medium and is replacing anhydrous ammonia in most of the Selective catalytic reduction (SCR) units. This newly developed model can estimate the vaporization rate and net mass evaporating into the air from a multicomponent non- ideal chemical spill. The work has been divided into two parts. In the first step a generic, dynamic source term model was developed that can handle multicomponent non-ideal mixtures. The applicability of this improved pool model for aqueous ammonia spills was then checked to aid in the offsite consequence analysis of aqueous ammonia spills.

The behavior of the chemical released depends on its various inherent properties, ambient conditions and the spill scenario. The different heat transfer mechanisms associated with the pool will strongly depend on the temperature of the liquid pool system at different times. The model accounts for all the temperature gradients within the contained pool and hence helps us establish better estimation techniques for source terms of chemical mixtures. This research work will help obtain more accurate and reliable liquid evaporation rates that become the critical input for dispersion modeling studies.

DEDICATION

To Amma, Daddy, Ashwin, Rajam Patti & Sethu Patti who have extended great love and support throughout my life

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my academic advisor, Dr. Sam Mannan, for his boundless motivation throughout my master's program. He has definitely been a source of inspiration and a role model in my life. I am also grateful to Dr. Michael Lindell and Dr. Mahmoud El-Halwagi for their cooperation and support. I also wish to thank Dr. William. J. Rogers for the insightful discussions I have had with him related to my research. I would also like to express my special thanks to Dr. Harry West for his timely help and excellent guidance. I also take this opportunity to thank Dr. Peck and Dr. Ganesan Gopalakrishnan for helping me get financial assistance. I am also grateful to all my wonderful teammates and the staff of the Mary Kay O'Connor Process Safety Center for all their help. I would like to extend my special thanks to Srini and Adhi for their immense help. I also owe a special thanks to Towanna and Ninette for helping me with all the paperwork throughout these two years. I also take this opportunity to thank all my nearest and dearest friends around the globe for all their support. Finally I once again thank my beloved parents and my brother who gave me an opportunity to realize my dreams.

TABLE OF CONTENTS

Page

ABSTRACT iii

DEDICATION iv

ACKNOWLEDGEMENTS v

TABLE OF CONTENTS vi

LIST OF FIGURES viii

LIST OF TABLES x

CHAPTER

I INTRODUCTION 1

1.1 Introduction 1
1.2 Chemistry Involved in NOx Reduction 3
1.3 Ammonia Injection System 4
1.4 Regulatory Implications of Ammonia Used in SCR Process 5

II OFFSITE CONSEQUENCE ANALYSIS 7

2.1 Introduction 7
2.2 Risk Management Plan for Industrial Facilities 7
2.3 Five-Year Accident History 10
2.4 Offsite Consequence Analysis Procedure 11
2.5 Emergency Response Program 15
2.6 EPA's Effort on OCA for Anhydrous Ammonia/Aqueous Ammonia 16

III SOURCE TERM MODELING 19

3.1 Introduction 19
3.2 Background 20
3.3 Pure Component Models 21
3.4 Multi-component models 24
3.5 Other Concepts 25

Page

CHAPTER

IV MODEL DETAILS 27

4.1 Introduction 27
4.2 Liquid Spill Characteristics 27
4.3 Characteristics of Chemical Emitted 28
4.4 Modeling Assumptions 29
4.5 Theoretical Basis for Models 30

V MODEL DEVELOPMENT 39

5.1 Introduction 39
5.2 Bulk Evaporation 39
5.3 Surface Evaporation 40
5.4 Improved Surface Evaporation Model 43

VI MODEL VALIDATION AND TESTING 45

6.1 Introduction 46
6.2 Base Case 46
6.3 Sensitivity Analysis 52
6.4 Validation Against Experimental Data 58
6.5 Validation for Other Chemicals 64
6.6 Applicability of the Model Under Different Meteorological Conditions 67
6.7 Limitations of the Model 69

VII MODELING SOFTWARE 70

7.1 Programming and Key Functions Used 70
7.2 Algorithm 72

VIII CONCLUSION AND FUTURE WORK 78

REFERENCES 80

APPENDIX A 83

APPENDIX B 89

APPENDIX C 97

VITA 100

LIST OF FIGURES

Page

Fig. 1. Simple cycle system....1
Fig. 2. Combined cycle system....1
Fig. 3. Low dust system....2
Fig. 4. High dust system....2
Fig. 5. Catalyst modules....3
Fig. 6. Reaction mechanism....3
Fig. 7. Ammonia injection process....4
Fig. 8. Flowchart for identifying the covered processes in the facility....8
Fig. 9. Steps for consequence analysis....12
Fig. 10. Generic source term modeling procedure....20
Fig. 11. Liquid pool mechanisms....31
Fig. 12. Comparison of non-ideality with Raoult's law case....34
Fig. 13. Mass flux of ammonia in air....48
Fig. 14. Cumulative mass of ammonia in air....49
Fig. 15. Cumulative mass of water vapor in air....49
Fig. 16. Surface temperature....50
Fig. 17. Bulk temperature....50
Fig. 18. Composition of ammonia in pool....51
Fig. 19. Partial pressure variation....53
Fig. 20. Mass flux of ammonia in air....54
Fig. 21. Effect of wind speed....55
Fig. 22. Effect of composition on partial pressure....56
Fig. 23. Effect of composition on surface temperature....57
Fig. 24. Experiment 1-Mass of ammonia in air....59

Page

Fig. 25. Experiment 2-Mass of ammonia in air....61
Fig. 26. Experiment1-Temperature gradients 62
Fig. 27. Experiment 1-Composition of ammonia....62
Fig. 28. Experiment 2-Temperature gradients 63
Fig. 29. Experiment1-Composition of ammonia....63
Fig. 30. Mass flux of ethanol....65
Fig 31. Mass flux of dichloromethane 67
Fig. 32. Matlab code....73
Fig. 33. Density of vapor cloud....87
Fig. 34. Meshed pool surface 92
Fig. 35. Top surface contour for a 10 cm pool depth 93
Fig. 36. Ground surface contour for a 10 cm pool depth 94
Fig. 37. Top surface contour for a 5 cm pool depth 95
Fig. 38. Ground surface contour for a 5 cm pool depth 96
Fig. 39. Quantity of HCN released into air 98
Fig. 40. Quantity of Acrolein released into air....98

LIST OF TABLES

Page

Table 1. Assumptions for modeling scenarios 16
Table 2. Base spill conditions 47
Table 3. Cumulative mass of ammonia in air 52
Table 4. Spill conditions for Mikesell et al. data 58
Table 5. Predicted values for experiment 1 59
Table 6. Predicted values for experiment 2 60
Table 7. Test conditions for Norman Dowell data 64
Table 8. Predicted values for ethanol 65
Table 9. Predicted values for propylene 66
Table 10. Meteorological conditions around the U.S. 68
Table 11. Test conditions for density validation 86
Table 12. Cloud density at different time instants 88

CHAPTER I

INTRODUCTION

1.1 Introduction

Nitrogen oxide (NOx) is one of the most common air pollutants and its removal technology has gained great importance from an environmental point of view. Selective Catalytic reduction (SCR) is the most commonly used technology for control of effective NOx emissions from utility boilers and combustion turbines nowadays (Pritchard et al. 1995). Its applications also include reduction of NOx emissions from diesel engines, process gas streams like nitric acid plants. The flue gas emitted from the refinery units need to be treated with a suitable catalyst under the presence of a reduction medium and ammonia serves that purpose in this process.

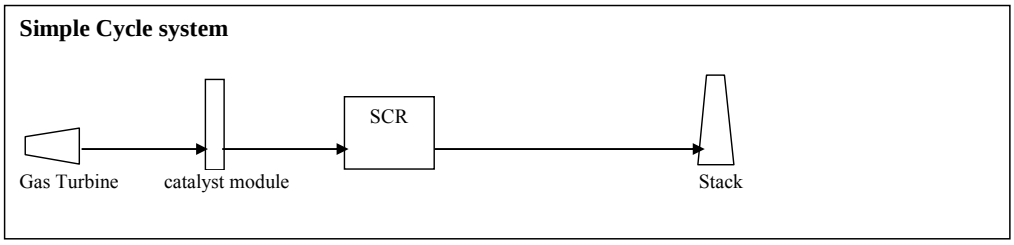

Fig. 1. Simple cycle system (Pritchard et al. 1995)

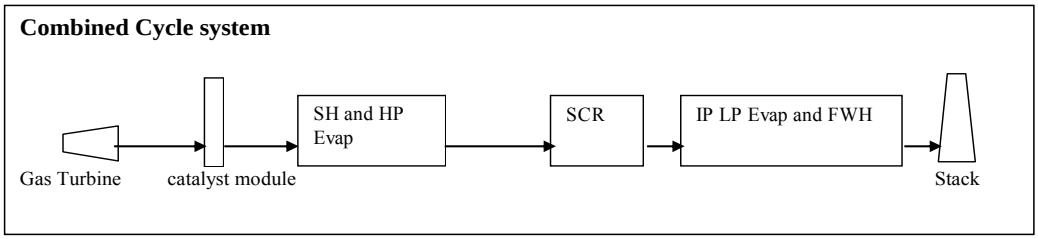

Fig. 2. Combined cycle system (Pritchard et al. 1995)

This thesis follows the style of *Journal of Environmental Engineering.*

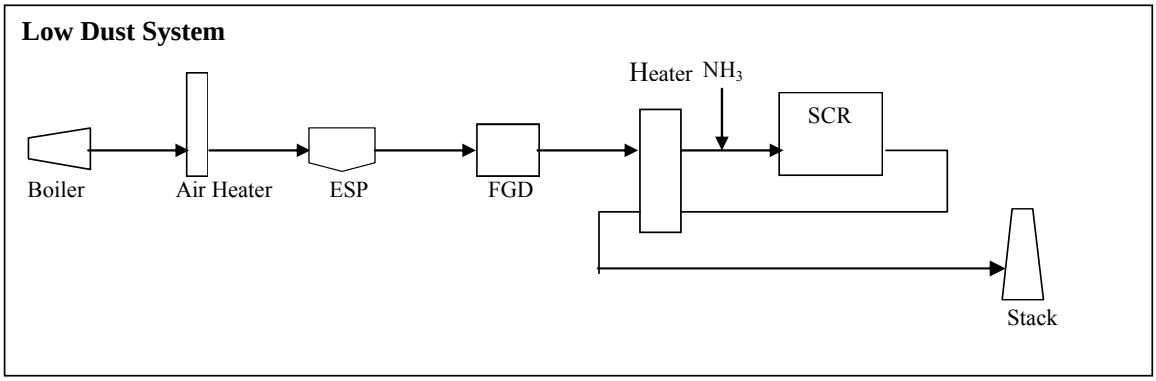

Fig. 3. Low dust system (Pritchard et al. 1995)

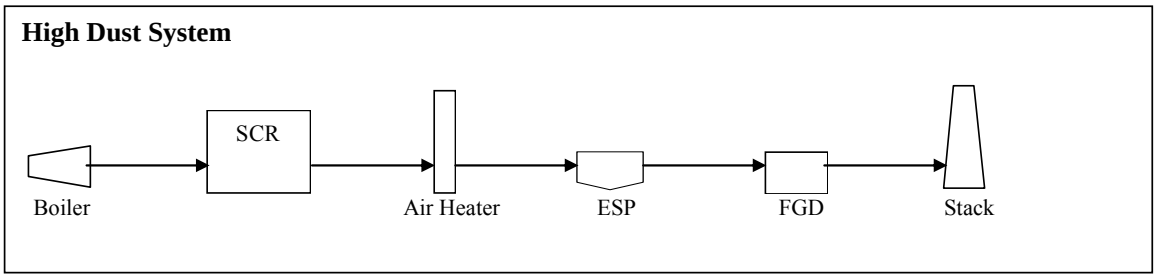

Fig. 4. High dust system (Pritchard et al. 1995)

This technology has proven to be the most economically viable solution, with cost estimates in the range of $20-$30 per kilowatt for natural gas units. In the above shown boiler SCR arrangements (Figures1-4) "NH_3" is the location of the ammonia injection grid, ESP is the electrostatic precipitator, FGD is the flue gas desulphurization unit, SH is the superheater, HP, IP, LP evap are the high, intermediate and low-pressure evaporator. The SCR equipment includes a reactor chamber, catalyst modules, ammonia storage system, ammonia vaporization and injection system, and monitoring equipment and sensors. The catalyst modules used in the SCR process is shown below (Figure 5).

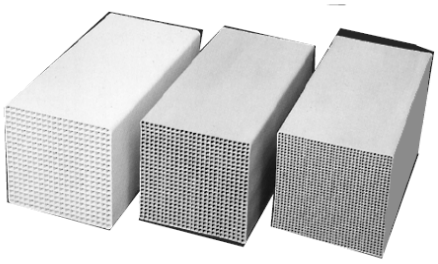

Fig. 5. Catalyst modules (Pritchard et al. 1995)

1.2 Chemistry Involved in NOx Reduction

The chemical reactions that take occur in the presence of the SCR catalyst, NOx reduction is as follows: (GEC, 1999)

$$NO + NO_2 + 2NH_3 \xrightarrow{catalyst} 2N_2 + 3H_2O$$

$$NO + 4NH_3 + O_2 \xrightarrow{catalyst} 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \xrightarrow{catalyst} 7N_2 + 12H_2O$$

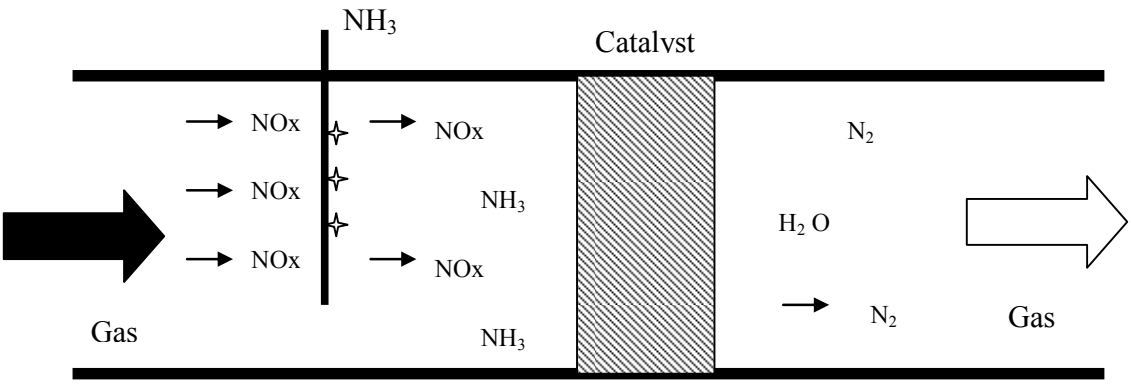

Fig. 6. Reaction mechanism (GEC, 1999)

The actual chemistry behind the reduction process is shown in Figure 6. The catalytic reaction can take place over a wide temperature range (300 deg F-1100 deg F) with typical applications between 500° F- 800° F. The ammonia also combines with the SO_3 gas to form ammonium sulfate salts and this could cause corrosion or plugging at times.

$$2NH_3 + SO_3 + H_2O \xrightarrow{catalyst} (NH_4)_2 SO_4$$

$$NH_3 + SO_3 + H_2O \xrightarrow{catalyst} (NH_4) SO_4$$

1.3 Ammonia Injection System

The aqueous ammonia stored in tanks is vaporized and mixed with air before it is brought into contact with the flue gas. The untreated gas and the oxygen rich ammonia mixture react with the gas in presence of a catalyst in the SCR chamber. The whole process can be represented as follows (Figure 7).

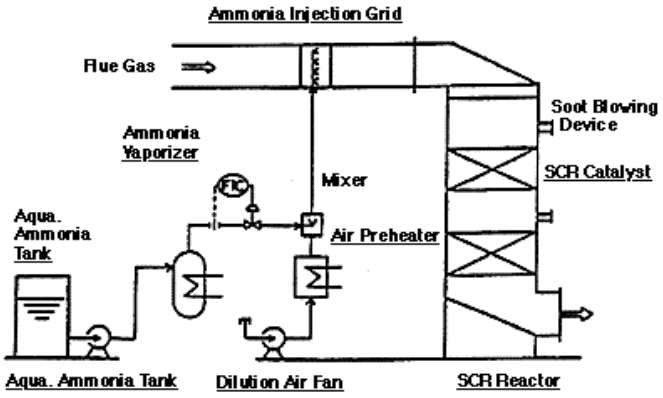

Fig. 7. Ammonia injection process (GEC, 1999)

Some of the advantages of using a SCR process in NOx removal process are

- Simple process
- Low running cost

- Easy operation
- No secondary environmental pollution
- High reliability
- High NOx removal efficiency
- Small pressure drop

1.4 Regulatory Implications of Ammonia Used in SCR Process

The ammonia used could be anhydrous or aqueous in nature. However anhydrous ammonia is being replaced by aqueous ammonia due to its more hazardous toxic effects compared to the latter. For comparing the potential impacts associated with an accidental release of ammonia some of the "bench mark" exposure levels need to be evaluated.

Threshold Limit Values: The American Conference of Governmental Industrial Hygienists (ACGIH) has established threshold doses called threshold limit values (TLV's) for a large number of chemical agents. The TLV usually refers to airborne concentrations that correspond to conditions under which no adverse effects are normally expected during a worker's lifetime. The exposure occurs only during normal working hours, eight hours per day and five days a week. The following are the definitions for all the TLV's used to commonly evaluate toxicity levels (Crowl and Louvar 2001)**.**

Threshold Limit Value -Time Weighted Average, (TLV- TWA): Time weighted average for a normal 8-hour workday or 40-hour workweek, to which nearly all workers can be exposed, day after day without adverse effects.

Threshold Limit Value –Short Term Exposure Limit, (TLV- STEL): The maximum concentration to which workers can be exposed for a period of up to 15 minutes continuously without suffering (1) intolerable irritation (2) chronic or irreversible tissue change (3) narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce worker efficiency, provided that no more than 4 excursions

per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded.

Occupational Safety and Health Administration -Permissible Exposure Level, (OSHA-PEL): (OSHA, 1992) OSHA sets permissible exposure limits (PELs) to protect workers against the health effects of exposure to hazardous substances. PELs are regulatory limits on the amount or concentration of a substance in the air. They may also contain a skin designation. PELs are enforceable. OSHA PELs are based on an 8-hour time weighted average (TWA) exposure. This value for ammonia has been set to 50 ppm.

Immediate Damage to Life and Health, IDLH: (NIOSH 2001) Occupational Safety and Health (NIOSH) in mid 1970's.This refers to a concentration, formally specified by a regulatory value, and defined as the maximum exposure concentration of a given chemical in the workplace from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects. The IDLH for ammonia is 300 ppm.

Emergency Response Planning Guidelines, ERPG: The ERPG-2 represents the concentration below which it is believed nearly all individuals could be exposed for up to one hour without irreversible or serious health effects (Crowl and Louvar 2001). The American Industrial Hygiene Association issues these ERPG values and for ammonia the standard ERPG-2 value is 200 ppm.

CHAPTER II

OFFSITE CONSEQUENCE ANALYSIS

2.1 Introduction

EPA's risk management program requirements may be found in Part 68 of Volume 40 of the code of federal regulations and it works with the industry, local, state and federal government agencies to assist sources in complying with the regulatory requirements. According to this rule if the facility handle, manufacture or store any toxic or flammable substances as listed in the appendix of 48 CFR Part 68,they are required to develop and implement a risk management program that includes a five-year accident history, an offsite consequence analysis, an accident prevention program and an emergency response program.

2.2 Risk Management Plan for Industrial Facilities

Environmental Protection Agency's (EPA) risk management program rule requires all the industrial facilities to perform a hazard assessment to provide information to the government and public about the potential consequences of a chemical release. Section 112(r) of the Clean Air Act (CAA) section directed the EPA to issue regulations for facilities with large quantities of very hazardous chemicals to prepare and implement programs to prevent the accidental release of these chemicals and mitigate the consequences of any releases that can occur (EPA 2004). In short, the objectives of this program are to prevent any serious damage to human health or environment and reduce the impact of such accidents that could otherwise have a severe consequence.

Applicability of the Risk Management Rule: Part 68 of the CFR in general applies to the owner of a stationary source (facility) that has more than a threshold quantity of a regulated substance in a process. The decision approach for identifying the covered processes is presented in the page below (figure 8).

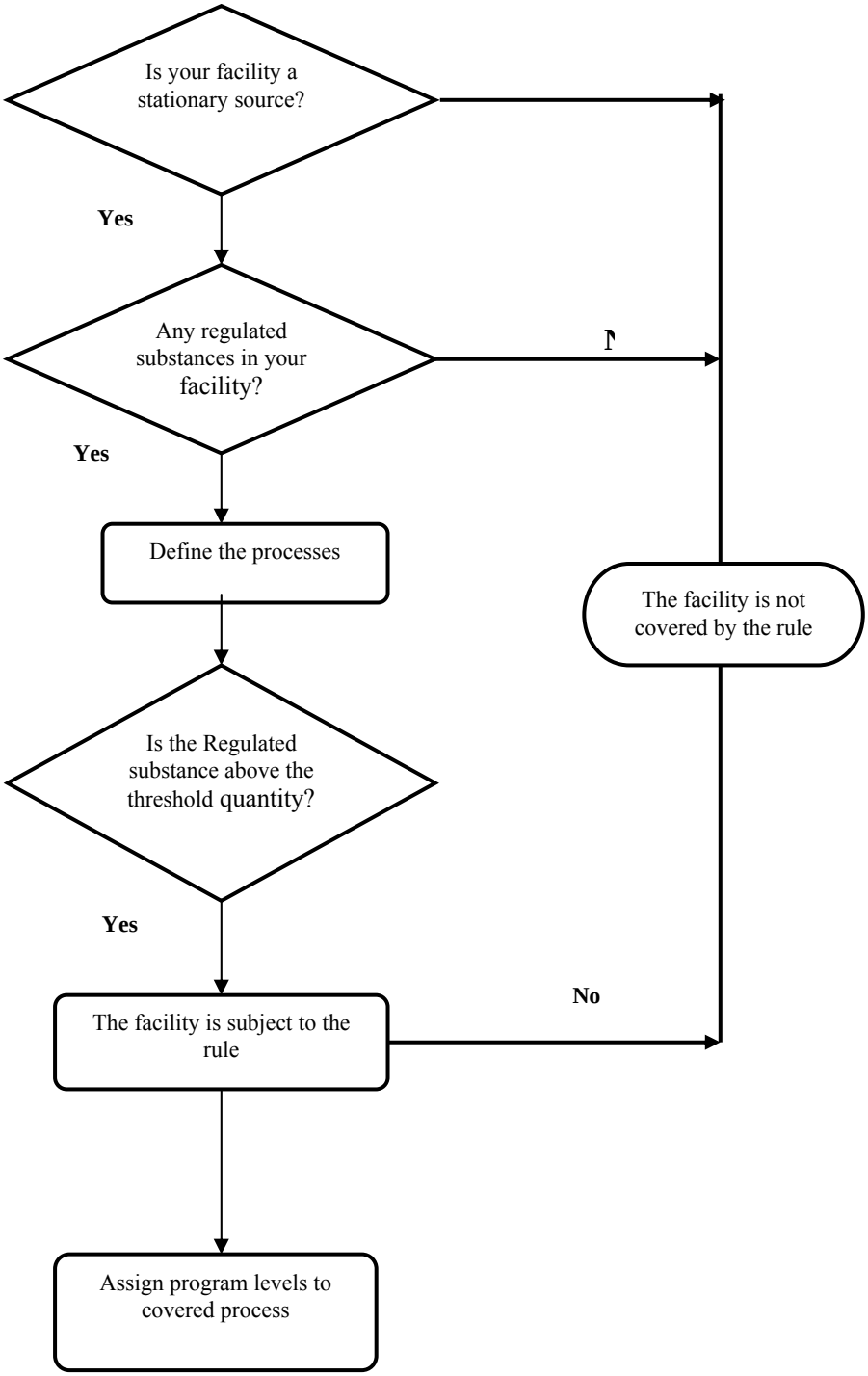

Fig. 8. Flowchart for identifying the covered processes in the facility, (EPA 1998)

Stationary Source (EPA 1998): CAA section 112(r) defines "stationary sources" as "Any buildings, structures, equipment, installations, or substance emitting stationary activities

- That belongs to same industrial group.
- That is located on one or more contiguous properties.
- That is under control of the same person.
- From which any accidental release may occur.

Regulated Substances: EPA has included a list of 77 toxic chemicals and 63 flammables that can cause serious health effects or have the potential to form vapor clouds and explode if released. The rule also includes those flammable mixtures that meet the criteria for the National Fire Protection Association. The rule applies only to those facilities that have one of those listed substances over 1 percent concentration or above their threshold quantities.

Process: Process again is defined as "any activity involving a regulated substance, including any use, storage, manufacturing, handling, or onsite movement such substances (EPA 2004).The flowchart needs to be followed to check if the facility is covered by the rule and at this stage program levels can be assigned to the processes. The program levels are defined as follows:

Program1: Processes that do not have public receptors within the distance to an endpoint from a worst-case release and no accidents with specific offsite consequences within the last five years are covered under Program1.The following points summarize the eligibility criteria for Program 1 coverage.

- A brief description of the worst-case release scenario, which must specify the vessel and substance selected as worst-case and modeling assumptions.
- Methodology used to determine the distance to endpoints.
- Data used to determine that no public receptor would be affected.

- Records showing the estimated quantity of worst-case release, release rate and duration of release.

This being the first or basic level imposes limited hazard assessment requirements.

Program 2: This is the default level because any covered process that is not eligible for Program1 or Program 3 is by default subject to Program 2 requirements.

Program 3: A process that is not eligible for Program 1 and meets one of the two criteria specified below can be subjected to Program 3 requirements.
The eligibility criteria for Program 3 are as follows:

- Process does not meet the eligibility requirements for Program 1
- Process is subject to OSHA PSM or process is one of the nine SIC codes.

2.3 Five-Year Accident History

The five-year accident history comprises of a detailed study of the effects of any accidental releases of one or more regulated substances from a covered process in those five years prior to the submission of a Risk Management Plan. The information on accidents should be collected for all processes that take place at the facility irrespective of whether its covered in Program1 or not.

2.3.1 Accident Reporting Criteria

There are some key points that need to be considered before actually including the accident/incident in the five-year accident history list. (EPA 1998)

- The release must be from a covered process and involve a regulated substance held above its threshold quantity in the process.
- The release must have causes at least one of the following
    - Onsite deaths, injuries or significant property damage.
    - Offsite deaths, injuries, property damage or environmental damage.

If the release of the regulated substance is below its threshold quantity it is not mandatory to report its release in the five-year accident history.

Information for the Five-Year Accident History: For every reported release the following data needs to be included.

- Date and Time of the accident/incident
- Release duration
- Quantity Released
- Nature of release (gas, liquid, aerosol, fire or explosion)
- Release source
- Weather Conditions
- Onsite impacts
- Offsite impacts
- Initiating event
- Changes introduced as a result of accident

2.4 Offsite Consequence Analysis Procedure

The basic steps involved in an offsite consequence analysis based on EPA guidelines are shown in a flowchart (Figure 9).

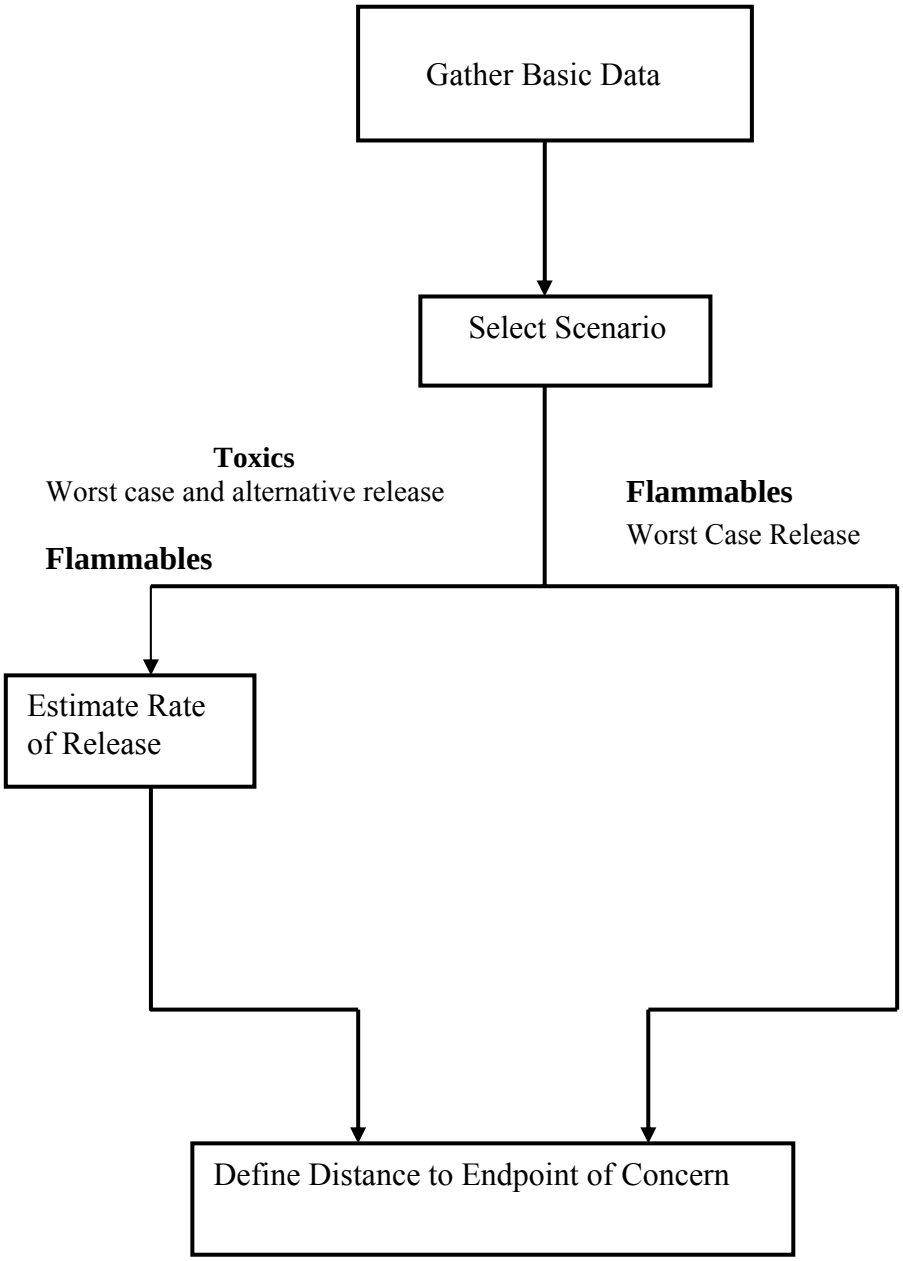

Fig. 9. Steps for consequence analysis (EPA 1998)

The first step of data collection depends on the process under consideration. Each process has its own characteristics that need to be identified to conduct the hazard assessment. Some of the process conditions are as follows:

Nature of the Chemical: The chemical needs to be classified as toxic, flammable or both based on its flammable properties and toxic exposure levels.

Temperature of the Chemical: The temperature of the chemical can be either at the inventory or during the process. Both these temperatures need to be noted as some reactive chemicals might behave completely different under high temperatures. Moreover at the modeling stage temperature becomes a very critical factor to estimate other physical properties that can determine the release rate.

Pressure of the Toxic/Flammable Chemical Used: Liquid pressure becomes very important as most liquids when stored under pressure above their boiling point temperature present substantial problems of flashing. The liquid leaking from a pipe or a tank can partially flash into vapor and can also be explosive at times.

Quantity of the Stored Chemical: The quantity of chemical handled again is a very important input for modeling the system. The quantity of substance can vary according to the scenario under consideration.

Active and Passive Mitigation Systems Present at the Process Site: Active mitigation is defined as equipment, devices or technologies that function with human, mechanical or energy input. Sprinkler systems, water curtains, valves and scrubbers are considered active mitigation systems. *Passive mitigation* systems are those that do not require any human, mechanical or energy input like dikes, building exposures and containment walls. The scenario selection procedure consists of two elements

A Worst-Case Release Scenario: It is defined as the release of largest quantity of a regulated substance from a single vessel or process line failure that results in the greatest distance to the toxic endpoint. The distance to the toxic endpoint is the distance a toxic

vapor cloud, heat from a fire or blast waves from an explosion will travel before dissipating to the point that serious injuries from short term exposures will no longer occur. The number of worst-case scenarios that need to be analyzed depends on the regulatory specifications on the toxicity and flammability of the substance.

Program 1 – Eligibility: The worst-case release scenario analysis is applicable to all covered process. For a process to be eligible for Program 1 the worst-case analysis should indicate that there are no public receptors within the distance to an endpoint. If there is more than one process that may qualify under this category a separate analysis needs to be performed to verify its eligibility.

Program 2 – Eligibility: If the distance to the endpoint in the worst-case analysis is equal to or greater than the distance to any public receptor, the process can be included in Program 2 or Program 3.And for all these processes one worst case analysis for the regulated toxic substance and one for the regulated flammable substance needs to be carried out.

Alternative Release Scenario: An alternative scenario must be picked with reasonable assumptions and the credibility of the scenario must be justified. It is not necessary to demonstrate greater likelihood of occurrence or carry out any analysis of probability of occurrence while choosing the alternative scenario.

Some examples of alternative release scenario will be as follows (EPA 1998)

- Transfer hose releases due to splits or sudden uncoupling.
- Process vessel or pump releases due to cracks, seal failure or plug failure.

Another critical assumption for alternative release scenarios is the presence of active mitigation systems such as interlocks, shutdown systems, firewater and deluge systems. It is required to analyze at least one alternative release scenario for each listed toxic

substance in Program 2 and Program 3, however no analysis is required for regulated substances in Program 1.

Estimation of Release Rate and Distance to Toxic End Point: This step is the most critical step in estimating the source term and predicting downwind dispersion distance. These models for a worst-case scenario and alternative case scenario have different assumptions and these are summarized in Table1 shown below. The appropriate source term and dispersion models that satisfy the U.S EPA criteria can be used to predict the intensity of impact of these accidental releases.

2.5 Emergency Response Program

For a facility having at least one Program 2 or Program 3 process, then it is recommended to implement an emergency response consisting of an emergency response plan, emergency response equipment procedures, employee training and procedures to ensure that the program is up- to-date. If a chemical facility is planning to respond to release of substances with their own employees, the response program must consist of the following elements (EPA 1998).

- Standard procedures to inform the public and other agencies about the release
- Documentation of proper first aid and emergency medical treatment necessary to treat human exposures, and

Table 1. Assumptions for modeling scenarios (EPA 1998)

Parameter	Worst Case	Alternative
Endpoints	**Toxic substances endpoints** • Specified in appendix A of 40 CFR Part 68. **Flammable substances endpoints** • Overpressure of 1 psi for vapor cloud explosions.	**Toxic substances endpoints** • Specified in appendix A of 40 CFR Part 68. **Flammable substances endpoints** • Overpressure of 1 psi for vapor cloud explosions. • Radiant heat of 5 KW/sq.m • Lower Flammability Limit for vapor cloud fires.
Wind speed	A wind speed of 1.5 m/sec and F stability class unless the local conditions are more severe.	Site-specific meteorological conditions will be used.
Ambient temperature and Humidity	For toxic substances, highest daily maximum temperature during the past 3 years and average humidity for the site.	Average temperature and humidity at the chosen meteorological conditions will be used.
Height of release	Ground level release for toxic substances	Depends on the release scenario.
Topography	Urban or rural topography will be used	Urban or rural topography will be used.
Dense or neutrally buoyant gases	Tables or models used for dispersion of regulated toxic gas must account for gas density.	Tables or models used for dispersion of regulated toxic gas must account for gas density.
Temperature of substance	For liquids, the highest daily maximum temperature or process temperature whichever is higher.	Substances may be considered to be released at the process or ambient temperature.

- Procedures and measures for emergency response
- Training for all employees in relevant procedures.
- Procedures for using, inspecting, testing and maintaining emergency response equipment.

2.6 EPA's Effort on OCA for Anhydrous Ammonia/Aqueous Ammonia

EPA gives some guidance to perform the OCA for regulated substances like anhydrous and aqueous ammonia.

Anhydrous Ammonia: In general anhydrous ammonia is stored as a liquid under pressure to be used in refrigeration systems. If the temperature and pressure are sufficiently high, and if there is a sudden release of ammonia, the release mixture will be two phases, a mixture of vapor and fine liquid droplets. The EPA thus conducted a comparative study for a worst-case release of anhydrous ammonia at rural site. The toxic endpoint for ammonia as specified in any RMP 200 ppm was taken as reference.

Offsite Consequence Analysis for Aqueous Ammonia: The facility using SCR techniques as discussed in the previous chapter store aqueous ammonia in storage tanks outside at atmospheric pressure. The ammonia used could be anhydrous or aqueous in nature. However anhydrous ammonia is being replaced by aqueous ammonia due to its more hazardous toxic effects compared to the latter and the principal difference between these chemicals in the context of atmospheric dispersion modeling is that the former chemical evaporates as a pure vapor, whereas the latter escaped as an aerosol. Aqueous Ammonia is stored in vertical or cylindrical storage tanks and it is usually placed inside a diked containment area. The ammonia solution will be a water solution and stored close to ambient temperature and the worst case release scenario involves the rupture of the ammonia tank, instantaneous spilling of their contents into the containment dike and the evaporation of ammonia from this surface. In this case the offsite consequence analysis needs to be carried out on based on the guidelines discussed above. For comparing the potential impacts associated with an accidental release of ammonia some of the "bench mark" exposure levels need to be evaluated**.**

*Exposure Values for Ammonia**:*** (NIOSH 2001)

- Immediate Damage to Life and Health, **IDLH**: 300 ppm
- Threshold Limit Value-Time Weighted Average, **TLV- TWA**: 25 ppm
- Threshold Limit Value-Short Term Exposure limit **TLV STEL**: 35 ppm
  Emergency Response Planning Guidelines, **ERPG-2**: 50 ppm
- Occupational Safety and Health Administration -Permissible Exposure Level, **OSHA- PEL**: TWA 50 ppm

In the case of aqueous ammonia (concentrations less than 20%) the risks of reaching these exposure values are much less when compared to anhydrous ammonia due to lower partial pressures in solution. According to the U.S Environmental Protection Agency's (EPA) 112(r) clean air act, all regulated sources are required to conduct an offsite consequence analysis for a worst-case release scenario involving regulated substances**.** The analysis of potential consequences of an accidental release of ammonia needs to meet the EPA's guidance on analyzing accidental chemical releases. The worst-case assessment will also require an additional dispersion modeling for which the most important input is the vaporization rate of the chemical. The following chapters will discuss the modeling technique based on the EPA's regulatory compliance procedures.

CHAPTER III

SOURCE TERM MODELING

3.1 Introduction

Source term modeling is the most critical part of any consequence modeling procedure. Most of the accidents involve release of hazardous chemical from the containment. The imitating event for these accidents could be a pipeline or vessel rupture, hole in a tank, pipe or a runaway reaction. The source term model basically gives us information regarding the rate of discharge, total quantity discharged and the state of discharge. The units used for source emission term will generally depend on the scenario or the type of the release. Typically, emission rate units are expressed in terms of mass per unit time per unit area.

The accidental releases of chemicals can further be classified as gas or liquid, instantaneous or continuous, from storage tanks or pipelines, refrigerated or pressurized, on land or water, confined or unconfined (Hanna and Drivas 1987). The four basic steps involved in determining the source emission rate are as follows:

- Determining the time dependence of release scenario
- Identifying the most applicable source model
- Gathering specific input data and physical properties necessary for modeling.
- Calculating the source emission rate.

The following flowchart in figure 10 will depict the important steps mentioned above and any source term modeling procedure will have to follow these guidelines for a systematic approach.

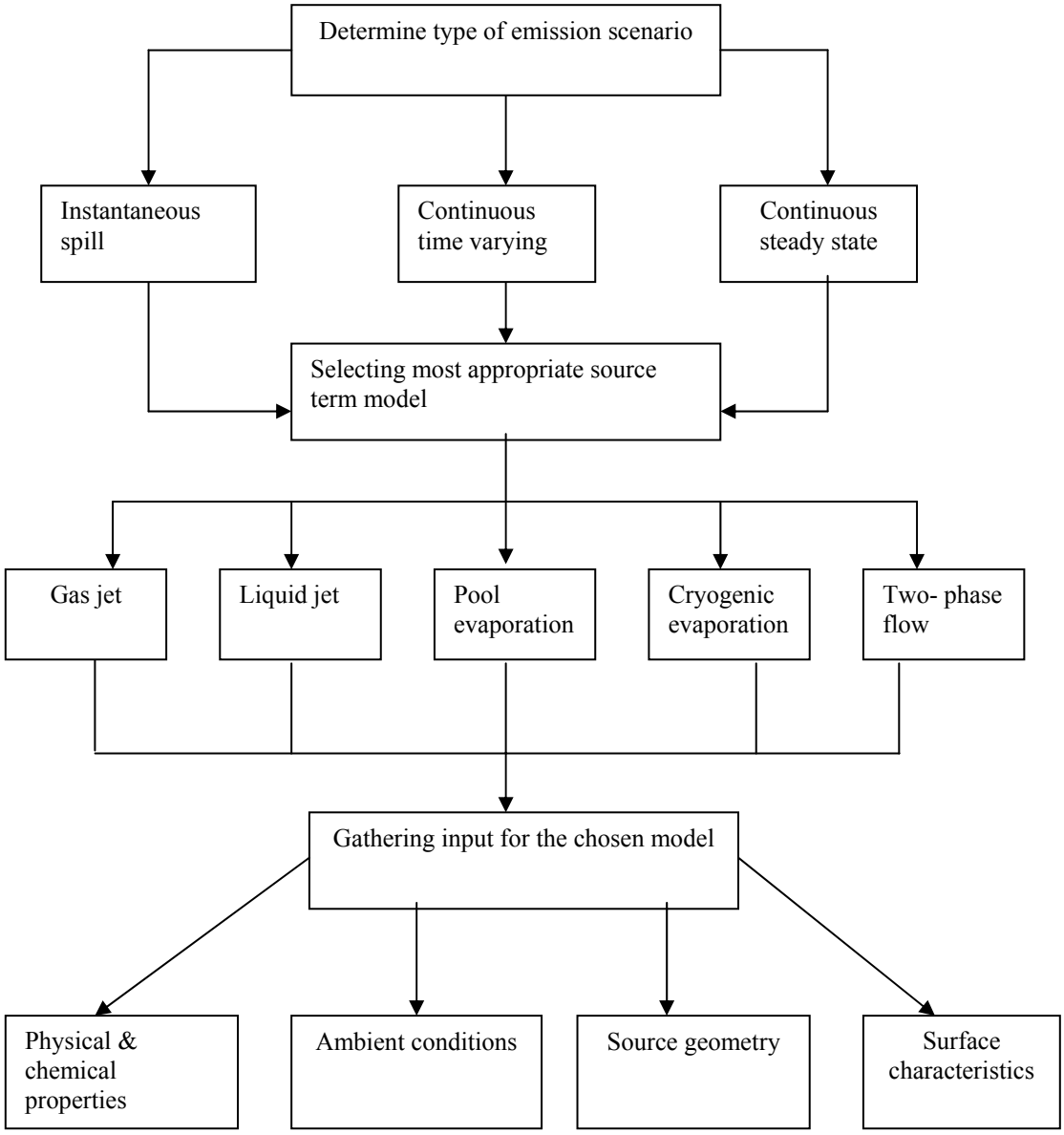

Fig. 10. Generic source term modeling procedure (Hanna and Drivas 1987)

3.2 Background

The concept of detailed source term modeling started as early as the 1970's.Several steady state, semi-empirical evaporation models are available which were programmed with minimum parameters. The models first developed only for pure component liquids

and were further developed over the years to suit chemical mixtures. Although many concepts were derived, only a few of them were actually made into user-friendly programs or simple equations that could be easily applied to practical situations. In this chapter a few important pure component and multi-component models will be reviewed to get a brief overview on the existing work in this field.

3.3 Pure Component Models

3.3.1 Ille and Springer Model (Ille and Springer 1978)

This model is considered to be the most sophisticated of all the models developed during the 1980's.In this model the evaporation rate is computed by the method of Mackay and Matsugu and is function of the concentration driving force as determined from vapor pressure. The liquid pool temperature is also assumed to be equal to the ambient temperature initially and is determined from a steady state energy balance equation at any other time. The model also assumes evaporation of a pure liquid and ideal gas behavior of the vapor film. These assumptions give a highly overestimated vaporization rate for the spilled liquids. The only special feature of this model was that the temperature inside the pool was tracked throughout the evaporation time and mass transfer coefficients were calculated based on that.

3.3.2 Army Model (Kunkel 1983)

This model was adapted from the Chemical Engineer's Handbook .The methodology used here computes source strength as a function of the Reynolds number, the Schmidt number, velocity of air and the vapor pressure of the pure chemical. The model gives a very approximate equation for determining the source term for liquids with Reynolds numbers less than 20,000.

$$Q = 0.3u^{0.8} A^{.0.9} T^{-0.8} (GMW)(Vp)\left[\frac{(3.1 + GMV^{0.33})^2}{T^{0.5}\left(\frac{1}{29} + \frac{1}{GMV}\right)^{0.5}}\right]^{-2/3} \qquad (1)$$

Q = Evaporation rate (kg/hr)

u = Wind speed (m/sec)

A = Area of spill (sq .m)

GMW = gram molecular weight of liquid

GMV = gram molecular volume of liquid at normal boiling point (cu.cm/g mole)

Vp = Vapor pressure of liquid (mm-Hg)

T = Temperature of the liquid (deg K)

The major limitations of this model are that it does not take into account the effect of evaporative cooling, radiation and further assumes pool temperature is the same as air temperature.

3.3.3 Shell Model (Fleischer 1980)

This is an unsteady state model that deals with the estimation of evaporation rates of pure chemicals. The model estimates the vaporization rate as a function of time. Even though it is a dynamic approach there is no heat transfer effect due to evaporative cooling and radiation. And moreover this model cannot be reduced to a simple expression like the Army model.

3.3.4 AWS Model (AWS 1978)

The air weather service (AWS) gives an empirical equation based on the laboratory studies for dinitrogen dioxide.

$$Q = K\, u^{0.8} A \qquad (2)$$

Q = Source strength (kg/hr)

u = Wind speed (m/sec)

A = Area of spill (sq .m)

K = A constant which is equal to the vapor pressure of the chemical.

The major deficiency of this model is its lack of dependency on temperature.

3.3.5 ALOHA (Mary et al. 1993)

ALOHA (Area Locations of Hazardous Atmospheres) is a computer program jointly developed by National Oceanic and Atmospheric Administration (NOAA) and U.S Environmental Protection Agency (EPA) that uses information you provide it, along with physical property data from its extensive chemical library, to predict how a hazardous gas cloud might disperse in the atmosphere after an accidental chemical release. This model uses the Kawamura Mackay relation for the mass transfer mechanism. The ALOHA package can be used to model a chemical puddle scenario and in this case the actual chemical, atmospheric conditions including surface roughness and the site location are taken into consideration to calculate the emission term. This information is then used to perform the dispersion the dispersion calculations.

However ALOHA is suited only for pure chemicals, a few select solutions and the property information in its chemical library is not valid for multicomponent mixtures. The model also displays the results only for 1 hour after the release takes place and does not predict vaporization rates at different time intervals. Moreover when an incorrect property value is used in ALOHA, the model's release rate and dispersion estimates will not be valid.

3.3.6 Raj Spreading Model (Raj 1981)

This model was developed in the early 80's to address the cryogenic liquid spills on water and land. In modeling spills on land the heat transfer rate is obtained from quassi one-dimensional theory. This model addresses both continuous and instantaneous spills. In both cases the model is derived by considering the hydrodynamics of the spread, the varying heat flux to the spreading liquid and the relation between them. The model also

assumes that the liquid pool spreads which is not necessary for instantaneous releases as the liquid quickly occupies the entire diked area. Further the various assumptions made in this model have not been well justified because of lack of experimental data for each of the situations considered.

All the above-mentioned models can calculate the source strengths only for pure chemicals or liquids. There are a few other multi-component models that were developed after this and some of the important ones are as follows.

3.4 Multi-component Models

3.4.1 Mikesell et al (Mikessell et al. 1991)

This model addresses the multi-component mixture spill and the model is transient in nature. The heat and mass balance equations are solved simultaneously to estimate the mass vaporization rate and the temperature. In this model various heat transfer mechanism are incorporated, however there is no proper justification for some of the assumptions. The model included condensation effects but it does not seem to show the behavior of vapor cloud in air to decide if condensation actually occurs. Moreover this model has not been programmed or made user friendly to enable to suit the end user.

3.4.2 CHEMMAP (McCay et al. 2003)

This model *predicts* the fate of a wide variety of chemicals products including floating, sinking soluble and insoluble chemicals and product mixtures. In this model the state and the solubility of the chemical are the most important factors. CHEMMAP is used for chemical spills on water surface to simulate slick spreading transport, evaporation and volatilization. The model actually uses the physical and chemical properties like density to predict the fate of a chemical spill.

CHEMMAP package is basically built of a chemical database, chemical fates model that estimates the distribution of chemical (as mass and concentrations), a stochastic model

that evaluates the probability of impact from a chemical discharge. This software runs with Applied Science Associates 'Geographic Information System (GIS). This model is more suitable for spill modeling to aid the evaluation of consequences of chemical spills on water.

3.4.3 LSM-90 (Cavanaugh et al. 1994)

This is a computer model and helps run simulations for vapor emissions from a multicomponent spill. This model is actually capable of handling boiling and non-boiling spills. The major assumptions of this model are that:

- All liquids and vapors are ideal
- The physical properties of the liquid will be averaged
- Multicomponent will always remain well mixed.

Some of these assumptions actually point out some drawbacks in the model. One of the major drawbacks of this model is that it is not capable of treating non-ideal mixtures that behave very differently when compared to the ideal solutions. However the model again does not take into account the temperature variation factor. Moreover the model is not very user friendly. This model currently needs to be run only in DOS mode that makes it difficult for the end user to interpret.

3.5 Other Concepts

Some other important concepts, which have been adapted into a few computer models, are described below.

3.5.1 Fay Model (Shaw and Briscoe 1978)

This model lays great emphasis on studying the effect of simultaneous spread and vaporization from spills of hazardous liquids water. However this model mostly concentrates on cryogenic spills like that of LNG. In this model it is assumed that the

initial gravitational potential energy is converted into kinetic energy. Fay also assumes that an ice layer is formed beneath the LNG and this plays a key role in the heat transfer mechanism. This model does not seem to be very applicable for instantaneous multicomponent mixture spills on land.

3.5.2 Lind Model (Shaw and Briscoe 1978)

Lind worked with instantaneous spills of 4000, 10,000 cu.m of LNG and studied the effects of chemical explosion that occurs after a large spill of LNG from a tanker. This model used an empirical pool spread rate and mass vaporization rate.

$$m = 175.7vt^3 \qquad (3)$$

where 'm' is the mass of chemical that evaporates and '*v'* is the mass flow rate and't' is the duration of spill.

3.5.3 GASP Model

GASP is an acronym for Gas accumulation over spreading pools and was developed by SRD/HSE. This model incorporates all the heat and mass transfer coefficients. However the temperature dependence of the source term is not discussed in detail in this model. Moreover the model has been converted to a computer program but is not very user friendly or interactive with current day applications.

All these models have some important drawbacks and more importantly they are not user friendly. The new model will have a more comprehensive approach and at the same will make some valid assumptions to make it generic in nature.

CHAPTER IV

MODEL DETAILS

4.1 Introduction

The liquid spill needs to be modeled with all the basic assumptions mentioned in the Risk management plan for industrial facilities. In the case of a chemical spill, the characteristics of the chemical have to be studied at all stages to develop the model.

4.2 Liquid Spill Characteristics

The liquid spilled on land will be emitted into the atmosphere depending on its physical properties and some extraneous factors. The spilled fluid characteristics depend on the following external factors:

4.2.1 Storage Tank

The chemical stored in facilities is usually stored in vertical or horizontal tanks. In some cases it may also be transported in pipelines in between the actual process in which it is involved. Source models are developed from fundamental equations that depict the physiochemical process occurring during the release of the material. The phase of the release also mostly depends on the storage tank conditions and the nature of release from the tank.

4.2.2 Presence of a Containment Dike

Passive mitigation systems like a containment dike serve a very important purpose while storing hazardous chemicals. As the liquid spills on the ground, they have a tendency to spread randomly as the gravitational force tries to balance the inertial force. A rectangular or circular dike around the storage tank can contain the spreading liquid. Moreover the release rate of the chemical is also reduced as the surface area for evaporation is reduced.

4.2.3 Characteristics of Spill Surface/Spill Geometry

The spill surface can be made of dry soil, concrete, insulated concrete and depending on the nature of the surface the chemical pool behavior changes with time. In the case of a contained liquid spill, the geometry of the bund is also important to model the heat transfer associated with the pool.

4.3 Characteristics of Chemical Emitted

4.3.1 Chemical Composition

The vaporized chemical can be a pure chemical, binary mixture, multicomponent mixture or even water solutions with very low concentration of hazardous chemicals. Most of the physical properties of these chemicals keep changing with their composition. For non-ideal solutions the physical property like vapor pressure are greatly influenced by the composition of the mixture.

4.3.2 Ambient Condition

Atmospheric conditions also play a very important role in predicting the vapor cloud behavior .The ambient temperature is a critical parameter for modeling the mixing of hazardous chemical with air. The cloud density can vary depending on the ambient temperature and this in turn will affect the end point concentration.

4.3.3 Spilled Chemical Conditions

Inherent properties like vapor pressure, density, and enthalpy of vaporization very clearly depend on the conditions of the pool. The temperature especially becomes the driving factor at one stage and the model needs to keep track of the temperature to predict accurate mass vaporization rates.

4.4 Modeling Assumptions

The chemical spill to be modeled needs some basic assumptions to reduce the complexity of the system. Most of these assumptions have been made in reference to the U.S EPA worst- case scenario modeling conditions.

- *Storage at Low Pressure*: The chemicals stored in the tanks are maintained at very low pressure almost close to atmospheric pressure. Liquids stored under high pressure above their normal boiling temperature present problems of flashing (Crowl and Louvar 2001)**.** For all other cases the spill is entirely in liquid form and there is a very negligible amount in the vapor phase.
- *Dynamics of the Release*: The release mechanisms may form an important part of source term modeling if chemical spill occurs due to a leak. However for instantaneous release, assuming worst-case scenario the dynamics will not affect the source term calculations.
- *Level Liquid Spill Surface*: The spill surface is flat without any dents or irregularities that could affect the surface area term used in calculating the mass flux.
- *Ground Does Not Absorb Spills*: Penetration of spilled material into the soil is a complex phenomenon to be incorporated into the model. Gravitational forces move the fluid into the soil at the same time capillary forces also influence the downward movement of the fluid. In this case the concrete is assumed to be impermeable to spilled chemical.
- *Composition of Air Does Not Change Significantly:* The composition of air should actually change as a new chemical is added to it. The properties that would be of interest will actually include cloud concentration, density and heat capacity. However the volume of air just above the pool when compared to the pool volume is in the range of 10-40 times more. Hence these property changes will not be very significant.

- *No Physical or Chemical Reactions:* For materials like ammonia, spills on land usually do not give rise to any reactions. However if the same spill were to take place on some water surface, ammonia undergoes a fast irreversible ionization reaction. (Raj 1980)

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH \rightarrow NH_4^+ + OH^-$$

Moreover ammonia is not found to be very reactive under extreme temperature conditions.

- *Ground Temperatures Remain Constant:* In most process industries, nowadays the diked area is made up of concrete pads. Further in these calculations the ground temperature is kept constant. This could be a valid assumption for spills taking place very close to the ambient temperature. In other cases the ground might actually cool down a bit and the heat flux to the pool will keep changing with time.

4.5 Theoretical Basis for Models

The basic modeling approach involves simultaneous heat and mass balances around the pool. The chemical spilled on land will usually have a huge volume of air above it and the ground at a particular temperature below it. Hence the mass emitted to the air above clearly depends on the mass transfer mechanisms and the heat transfer mechanisms involving the liquid pool, air and the ground. However in this case the energy and mass transfer mechanisms are coupled and hence their equations also need to be solved simultaneously. The figure 11 shown below clearly shows the various heat transfer mechanisms around the pool that need to be analyzed.

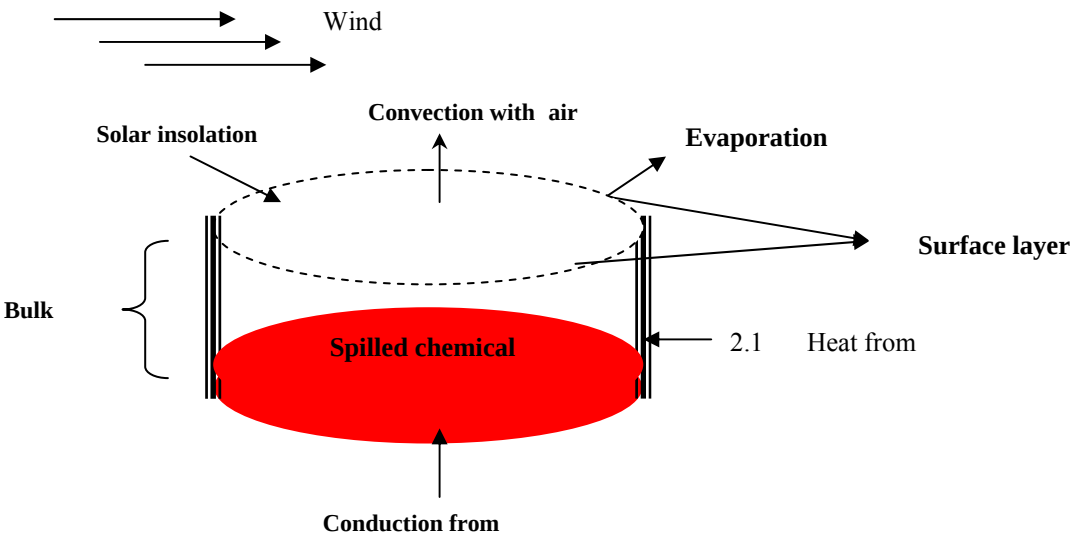

Fig. 11. Liquid pool mechanisms

4.5.1 Mass Transfer Mechanism

Bulk movement of each volatile component will occur as air flows over the pool. The mass transfer process can be explained in two parts.

Liquid Phase Resistance: The liquid phase mass transfer resistance affects the rate of transfer of chemical from the bulk of the liquid to the interface and this phenomenon takes into account the eddy and molecular diffusivities in the liquid (Mackay and Matsugu 1973)**.** For multi-component solutions there are two limiting conditions that may exist, one in which there is an infinite diffusion rate, the vapor leaving the surface will be in equilibrium with the bulk liquid. The other limiting condition is where there is no diffusion and the concentration of the mixture remains constant with respect to time and depth. In actual cases there exists an intermediate situation that drives the evaporation.

Vapor Phase Resistance: The second phenomenon is the vapor phase resistance that controls the rate of emission of chemical into the air. In this model vapor phase resistance is given more importance and an empirical correlation will be used for the mass transfer coefficient. This coefficient is a function of the molecular diffusion characteristics and expressed in terms of the Schmidt number. Moreover the theoretical modeling work by Dr Frie et al (Frie et al. 1992) shows that there is very little effect on the calculated vaporization rates from liquid phase resistance. Hence the assumption that vapor phase resistance is the driving force for mass transfer mechanism can be well justified.

For a multi component mixture each component moves depending on their partial pressures. Further the partial pressure changes with the temperature of the pool and hence becomes a dynamic property. The bulk transfer of fluid from the pool to the air flowing above it is given by

$$\frac{dm_i}{dt} = K_{mi} * A * MW * (P_s^i - P_a^i) / R * T_{pool} \qquad (4)$$

K_{mi} = Mass transfer Coefficient

A = Diked Containment area.

MW = Molecular weight of the components.

P_s^i =Partial pressure of the components in solution.

P_a^i =Vapor pressure of the components in air.

T_{pool} =Temperature of the pool.

R = Gas Constant

m_i =Mass flow rate of the components.

Here K_{mi} (mass transfer value) is an empirical value and can be calculated using the Schmidt number as shown below.

$$K_{mi} = \frac{0.0292 * u_w^{0.76} * d_o^{-.011} * Sc_i^{-0.67}}{RT_{pool}}$$

d_o =Pool diameter

u_w =Wind velocity

The average Schmidt number Sc_i is a function of the diffusivity of the component in air

$Sc_i = V_a / (d_a * D_i)$

The diffusivity D_i of each component in turn can be calculated by the Wilkey Lee method (Reid and Sherwood 1966).

V_a =Viscosity of air

d_a = density of air

The mass transfer equation 4 shown above represents mass transfer limited liquid pool evaporation. For liquid pools containing mixtures of liquids of varying volatility, the light components will evaporate first.

Partial Pressure Estimation: The partial pressure of each component in solution will depends on its interaction with other components in solution. For ideal systems it is usually done using the Antoine equation where the molecules virtually do not interact with other particles. In the case of non-ideal multicomponent mixtures like aqueous ammonia the ideal system assumption will actually introduce a great deal of error in the estimation of source term. The following graph will show how Raoult's approximation can overestimate the partial pressure of ammonia.

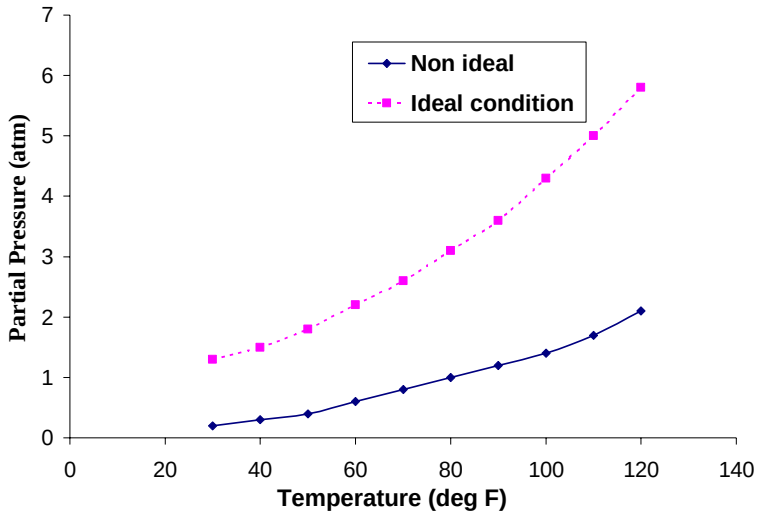

Fig. 12. Comparison of non-ideality with Raoult's law case

The figure above (Figure 12) shows that the ideal solution approximation predicts values with almost 200% error. This error will be carried on to the source term estimation if Raoult's law is applied for aqueous ammonia. Hence partial pressure data from standard books or an empirical relation needs to be used.

4.5.2 Energy Transfer Mechanism

The volatile components of the pool evaporate as heat is added to the pool continuously from various energy sources. The initial storage conditions of the pool (temperature, pressure) suggest that the pool does not boil and mass loss takes place only due to vaporization. The net energy balance around the pool can be represented by the following equation.

$$Q_{\text{air}} + Q_{dike} + Q_{\text{evap}} + Q_{\text{ground}} + Q_{\text{rad}} + Q_{\text{sensible}} + Q_{\text{sun}} + Q_{\text{mass-add}} = 0 \qquad (5)$$

However to calculate each heat transfer property we would need to calculate some physical properties. All these basic or relevant heat transfer mechanisms shown in figure 11 can be explained in detail as follows.

Ambient Heat Convection: The rate of convective heat transfer from the pool to the air above it is given by the following expression

$$Q_{air} = h * A * (T_{ambient} - T_{pool}) \qquad (6)$$

h = Heat transfer coefficient, calculated from heat and mass transfer analogy

A = Pool Area

$T_{ambient}$ =Ambient temperature

T_{pool} =Pool temperature

The data on heat transfer coefficient 'h' from atmosphere to water is very limited. An empirical relation for the heat flux due to convection derived from experimental correlations developed for LSM-90 model (Cavanaugh et al. 1994) has been utilized in this new model.

$h = K_{mi} * d_a * C_p * (Sc_{av}/Pr)^{0.67}$

d_a = Density of air

C_p = Specific heat of air

Pr = Prandtl number

Sc_{av} = Average Schmidt number

Where 'K_{mi}' is the mass transfer coefficient, it is an empirical value that solves a steady state atmospheric diffusion equation with power-law vertical velocity and eddy diffusivity profiles.

Heat from Dike: The heat added from the dike can be included depending on the area and the nature of the dike (insulated or non-insulated). It might not be very significant in many cases. The energy transfer phenomenon across the solid wall boundary is usually

conduction. The equation shown below is basically derived from Fourier's law of heat conduction.

$$Q_{dike} = \sum_{i=0}^{N} \frac{\left[2 * k * (T_{dike} - T_{pool}) A_i\right]}{(\sqrt{\prod * \alpha}) * (\sqrt{t} - \sqrt{t_i^*})} \qquad (7)$$

K = Thermal conductivity of ground

α = Thermal diffusivity

t = Time in seconds

t_i^* = Time section 'i' was first wetted in seconds

A_i = Area of the section of dike in contact with the liquid.

T_{dike}=Temperature of the dike

Heat from the Ground: The heat added from the ground can be added depending on the surface area and material of the ground. In this case energy is transferred across the ground by means of conduction. The equation shown below is also derived from Fourier's law of heat conduction. The rate at which heat is transferred is based on major assumption that the ground temperature does not vary throughout the vaporization process.

$$Q_{ground} = \sum_{i=0}^{N} \frac{\left[2 * k * (T_{ground} - T_{pool}) A_i\right]}{(\sqrt{\prod * \alpha}) * (\sqrt{t} - \sqrt{t_i^*}} \qquad (8)$$

T_{ground} =Temperature of the ground.

The remaining terms in this expression have the same definition as mentioned in the "Heat of dike" expression mentioned above.

Heat from Evaporation: As the pool loses chemical to the air above it, there is also some substantial amount of energy that is carried away by this vaporizing chemical. This directly causes the pool temperature to fall and this effect is known as evaporative cooling.

$$Q_{evap} = \sum \left(m_j * \Delta H_{vapj} \right) \tag{9}$$

m_j = Rate of evaporation of component j.

ΔH_{vapj} = Heat of vaporization of component j.

This heat of vaporization value can be calculated using the Pitzer –Accentric factor correlation. (Reid and Sherwood 1966)

Heat of the Material Added: This term is added to incorporate the energy transfer associated with the material that spills into pool. This energy term is more applicable for a system where there is continuous liquid spill over a substantial period of time.

$$Q_{mass-add} = m_{pool-input} (T_{storage} - T_{pool}) \tag{10}$$

where,

$m_{pool\text{-}input}$ = mass entering the pool at any time.

$T_{storage}$ = Temperature of stored chemical

Radiative Heat Transfer: The heat transferred from the atmosphere, as a long wave radiation and short wave radiation need to be incorporated into the energy balance equation. However a constant value 130 Btu/hr-ft^2 can be used (Studer et al. 1988). Moreover it has been found that this term is very small in energy balance calculations when compared to other heat flux terms.

Sensible Heat: The sensible heat added to the pool represents the accumulation term in a general heat balance. This term balances the remaining heat flux terms in the net energy balance equation. For highly volatile compounds, due to evaporative cooling effect this term will be negative indicating the drop in pool temperature.

$$Q_{sensible} = m_{pool}\, c_p\, (T_{pool} - T_{pool\text{-}prev}) \qquad (11)$$

$T_{pool\text{-}prev}$ = Temperature of the pool at the previous time instance (t-1)

The pool evaporation model that will be developed in the next chapter will incorporate these basic heat and mass transfer principles and will be improved step by step.

CHAPTER V

MODEL DEVELOPMENT

5.1 Introduction

At this stage, with all the basic mass and heat transfer mechanisms associated with the liquid pool being identified, a systematic approach has been adopted to first develop a basic pool evaporation model and then improvise it.

5.2 Bulk Evaporation

As the chemical spills on to the land, it tries to equilibrate within a few minutes and after which the various energy transfer mechanisms can be applied. At this stage most of the critical heat transfer methods involve the temperature of the pool. The liquid pool can be treated as a stagnant layer of fluid that interacts with the atmosphere and the ground. The basic energy balance expression from equation 5 will be used again to discuss this section

$$Q_{\text{air}} + Q_{dike} + Q_{\text{evap}} + Q_{\text{ground}} + Q_{mass-add} + Q_{\text{rad}} + Q_{\text{sensible}} + Q_{\text{sun}} + Q_{\text{tank}} = 0$$

5.2.1 Convection in Air

The pool temperature directly affects this term as shown in the following proportionality expression

$$Q_{air} \propto (T_{ambient} - T_{pool})$$

Any small change in this term will affect the energy transferred across the air-pool interface and this in turn will affect the mass of chemical vaporized from the pool. Hence the model should track the pool temperature at every time instant.

5.2.2 Ground Energy Transfer Term

Similar to the ambient convection term the interaction with the ground also has direct relation with pool temperature. However, in this expression the ground temperature remains constant and the heat flux will again depend only on the pool.

$$Q_{ground} \propto (T_{ground} - T_{pool})$$

5.2.3 Evaporation Energy Term

This mechanism is the most important since it accounts for most of the heat loss from the pool. The evaporative energy causes the pool to cool down continuously and this effect becomes very prominent for non-ideal liquids where the heat transfer properties are a strong function of temperature.

All the three mentioned transfer mechanisms play a very important role in determining the temperature of the pool at different time instants once the evaporation begins. In this bulk evaporation method the liquid pool is treated as a semi-infinite slab and evaporation is assumed to take place from the pool as a whole. There is no mechanism that accounts for the mixing inside the pool. The heat transfer is based on average pool properties with no temperature gradients across the pool.

5.3 Surface Evaporation

In this approach the whole pool will be divided into two layers, one being the surface and the other known as the bulk. The surface of the pool is an infinitesimal layer of pool from which evaporation actually takes place. The layer below this surface is of considerable thickness and actually interacts with the ground and also supplies heat to the surface above.

5.3.1 Pool Surface Conditions

The surface on top acts like a cap for the pool bulk and is at a slightly lower/higher compared to the layer beneath it. The heat transfer equation for the surface can be written as shown below.

$$Q_{sun} + Q_{air} + Q_{bulk} + Q_{sensible} = Q_{evap} \qquad (12)$$

The above expression is derived from the basic heat transfer equation written for the bulk evaporation method. The new term 'Q_{bulk}' represents the energy transferred across the bulk – pool boundary. As small amounts of the components vaporize from the top of the pool, they are immediately replaced by the contents of pool below it .The process involves some amount of energy transfer from the bulk to the surface. The surface of the pool acts like a blanket and is at different temperature from the bulk of the pool and this bulk heat transfer term is also critical in determining the actual energy transfer that occurs. The expression for bulk heat transfer is represented as

$$Q_{bulk} = h_{bulk} (T_{bulk} - T_{surface})$$

'h_{bulk}' is the heat transfer coefficient and can be estimated using the following relation derived by Kawamura and Mackay.(Kawamura and Mackay 1987)

$$h_{bulk} = k_{liq} / (h * \varphi)$$

T_{bulk} =Bulk pool temperature

$T_{surface}$= Temperature of the surface.

k_{liq} = Average thermal conductivity of the liquid.

h = Depth of pool at any instant of time.

φ = Liquid resistance factor.

The liquid resistance factor can be defined by the following expression.

$$\varphi = 1 + \exp(-0.6(T_{boiling,av} - 343.16))^{-1}$$

Where $T_{boiling,\ av}$=Average boiling point of the mixture.

The liquid resistance factor takes into account the relative role of conduction heat transfer vs. eddy transfer. If conduction dominates φ tends towards 0, otherwise φ tends towards 1 and conduction becomes important. For most non-cryogenic materials it has been observed conduction starts dominating after the first few minutes**.** (Raj 1980)

5.3.2 Pool Bulk Conditions

The bulk of the pool, just below the surface layer will also have some energy mechanisms associated with it. When the pool contents evaporate, they are replenished to the top from this layer of the pool. However in this surface evaporation model, the temperature in the bulk of the pool is averaged out and hence $\frac{\partial T_{bulk}}{\partial z}$=0. The heat balance in the bulk of the pool is given as follows in equation 13.

$$Q_{dike} + Q_{ground} = Q_{bulk} \qquad (13)$$

Q_{bulk} = Bulk heat transfer due to conduction through liquid.

T_{bulk} =Temperature of the Bulk.

z = Depth of the pool.

In this model, solving the equation for mass transfer, surface and the bulk heat transfer e simultaneously will solve the energy balance equation. All three mechanisms that take place are coupled and need to be solved iteratively to estimate the mass vaporization rate and the temperature gradients in the pool. The most important common term in all three equations will be the temperature of the pool and this varies with time. A small change in the bulk temperature will affect 'Q_{bulk}' and will in turn affect the mass of the contents

vaporizing from the top. These equations being time dependent can be solved for any amount of time provided the whole of the spill does not evaporate before the iteration time.

5.4 Improved Surface Evaporation Model

The slightly modified "surface evaporation approach" described above clearly shows the temperature sensitivity of the model. Now the bulk of the pool beneath the surface can be further divided into a number of planes of very small thickness. This approach will assume that there is a temperature gradient along the depth of the pool. This allows us to estimate the exact temperature of the bulk layer just below the surface layer and the heat transfer across bulk- surface boundary can be further enhanced improved by using a better temperature average.

5.4.1 Surface Conditions

In this approach, initially the energy balance for the surface can be represented with a more basic equation where temperature of surface changes with time and depth.

$$\rho c_{p.} h. \frac{\partial T_{surface}}{\partial t} = -k \frac{\partial T_s urface}{\partial z} + Q_{sensible} + Q_{bulk} + Q_{air} + Q_{sol} - mH_v \quad (14)$$

The equation 14 has been derived from the basic heat transfer equations for stationary sources (2000). However the pool surface has been defined as an infinitesimal layer or as a fluid layer of negligible thickness and this assumption will help us eliminate the $-k \frac{\partial T_s}{\partial z}$ term and the above written equation reduces to:

$$\rho c_{p.} h. \frac{\partial T_s}{\partial t} = Q_{sensible} + Q_{bulk} + Q_{air} + Q_{sol} - mH_v \quad (15)$$

All the energy terms other than the flux term are the constant heat source terms. This differential equation can now be solved with a pseudo equilibrium assumption. This assumption will hold good for very small time steps.

5.4.2 Bulk Conditions

For the bulk case, the temperature can be tracked by accounting for the different mechanisms as mentioned in the surface evaporation method. The major assumption in this model is that conduction dominates after a certain amount of time. However this model is different from the surface evaporation in that it accounts for bulk temperature variation in the vertical plane.

$$\rho c_{p.} h. \frac{\partial T_{bulk}}{\partial t} = -k \frac{\partial^2 T_{bulk}}{\partial z^2} \qquad (16)$$

ρ = Bulk density of the pool

c_p = Specific heat capacity of liquid

k =Thermal conductivity

h = Initial depth of pool.

The above written equation for the bulk of the pool can be solved with suitable boundary and initial conditions.

Initial Condition

At $t=0$, $T_{bulk}(z, 0) = T_{surface}$

Boundary condition

At $z=0$, $-K\frac{\partial T_{bulk}}{\partial z} = Q_{ground}$

At $z= h$, $-K\frac{\partial T_{bulk}}{\partial z} = Q_{bulk}$

These partial differential equations will be solved with respect to time and pool depth and the bulk temperature will be represented as a function of both. Now the plane just below the surface will be considered to average out the bulk temperature instead of the whole pool. This will further enhance the flux calculations across the surface –bulk boundary and will help predict better source terms.

CHAPTER VI

MODEL TESTING AND VALIDATION

6.1 Introduction

The improved model will now be demonstrated and validated to predict source term values under different set of conditions. The whole validation process will be divided into four stages.

- Aqueous ammonia base case demonstration.
- Sensitivity analysis will be conducted to test the performance of model under different conditions.
- Validation against experimental data will be performed to check the confidence of the predicted values.
- The model will also be tested for other chemicals and their experimental results

6.2 Base Case

Aqueous ammonia spill on to a diked containment area will be modeled with a particular set of parameters and the various results obtained from this simulation will be presented to discuss the applicability of this model to our case. The spill temperature will be assumed to be equal to the ambient temperature. The Table 2 presented in the next page will summarize all the spill parameters.

Table 2. Base spill conditions

Aqueous Ammonia weight (%)	Ground temperature (deg K)	Ambient temperature (deg K)	Air velocity (m/sec)	Relative Humidity (%)	Duration of spill (hours)
28	297	302	5	50	3

The time dependent unsteady state approach will help analyze the results in a more detailed fashion. The dynamic code was run under the following conditions and the following outputs were generated for the pool.

- Mass flux of ammonia vapor
- Cumulative mass of ammonia and water in air
- Temperature of the surface
- Bulk temperature gradients along the depth of the pool
- Composition of the pool

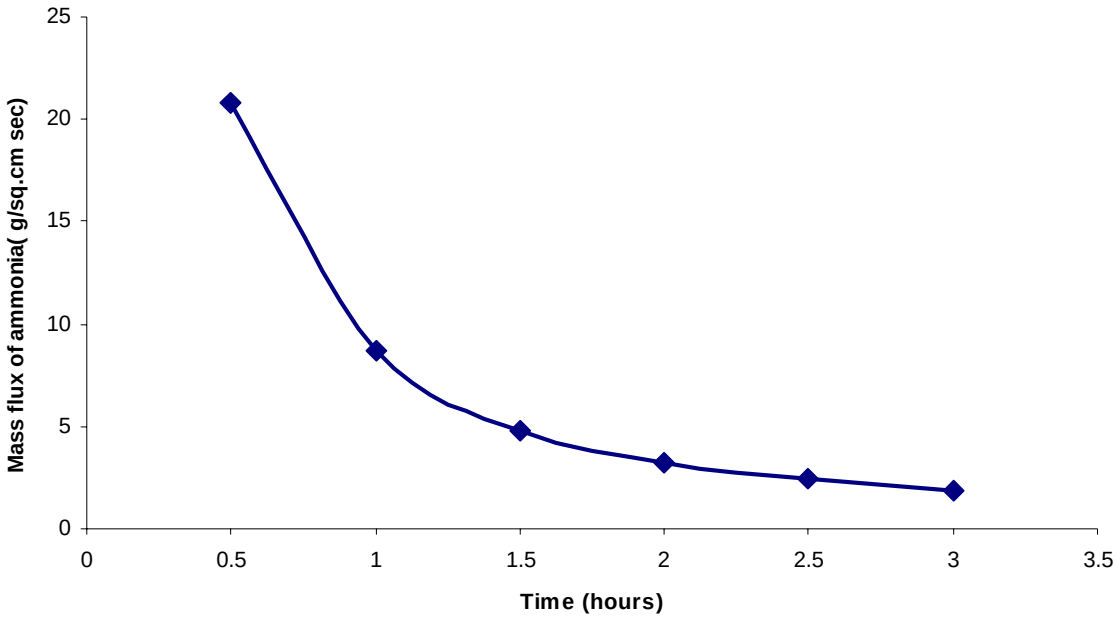

Fig. 13. Mass flux of ammonia in air

The vaporization rate of ammonia is clearly diminishing with time (Figure 13) and this behavior is consistent with the fact that vapor pressure decreases as evaporation proceeds. The plot of cumulative mass of both chemicals ammonia and water (Figures 14 and 15) are shown below to determine the chemical composition in air.

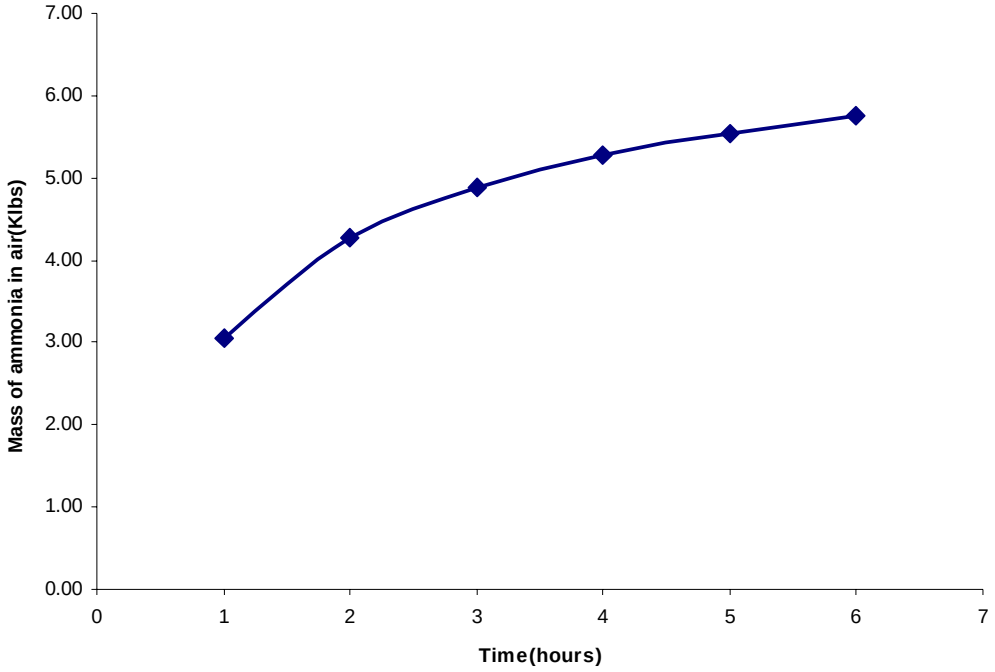

Fig. 14. Cumulative mass of ammonia in air

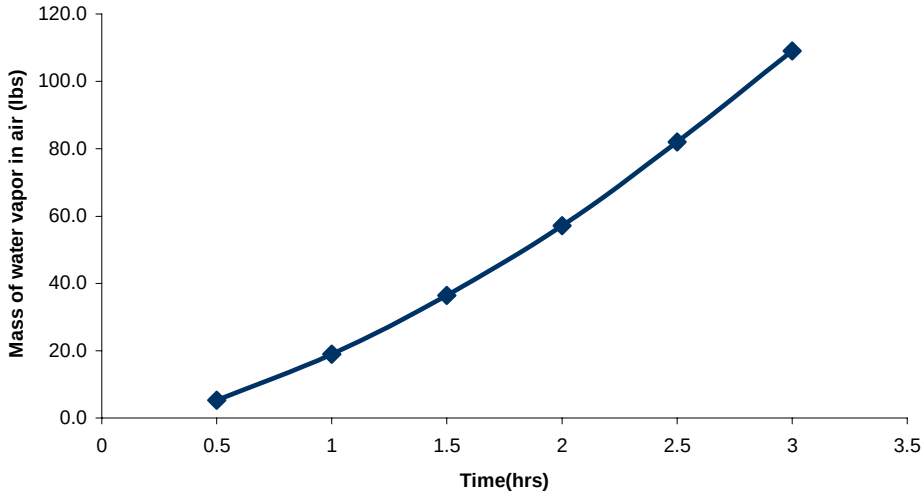

Fig. 15. Cumulative mass of water vapor in air

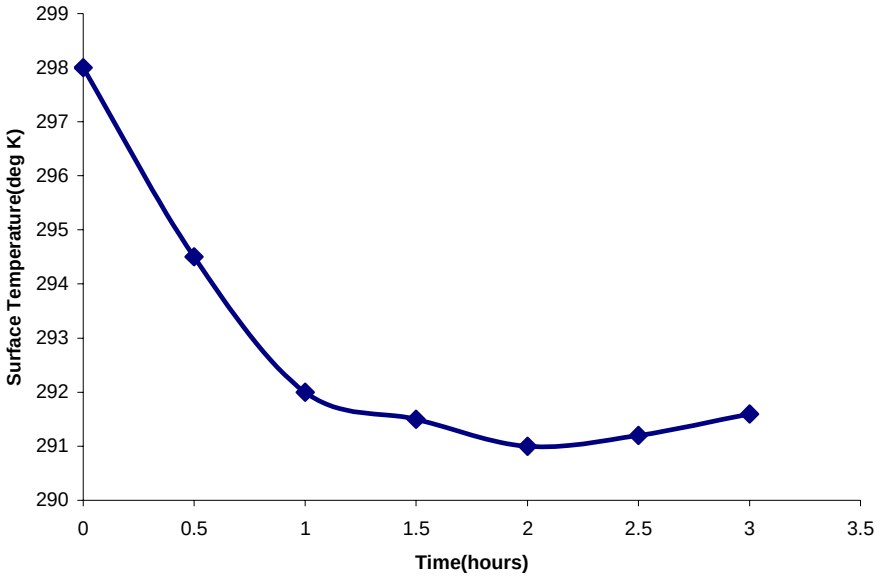

Fig. 16. Surface temperature

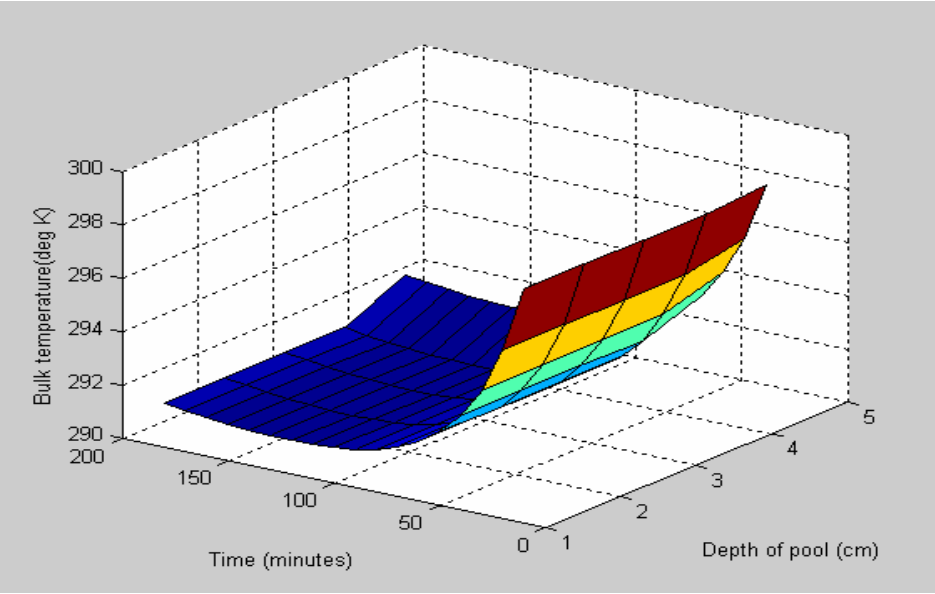

Fig. 17. Bulk temperature

It can be seen from the above plots (Figures 16 and 17) that surface temperature and the bulk temperature drop with time and this can be directly attributed to the evaporative cooling effect.

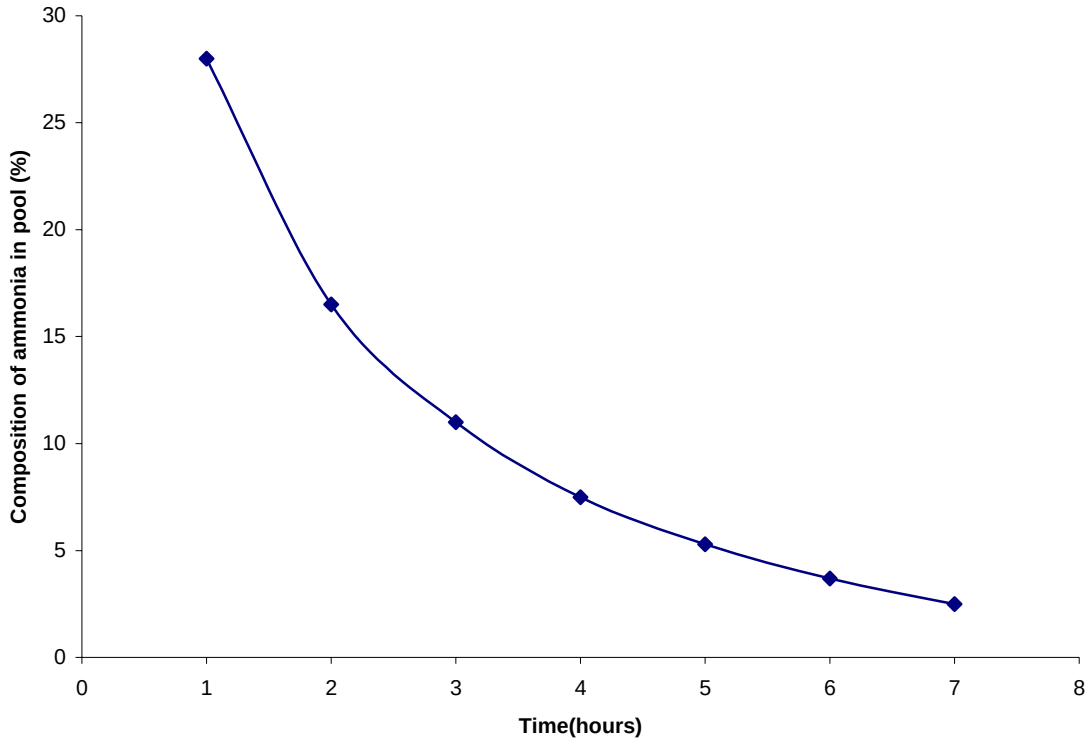

Fig. 18. Composition of ammonia in pool

The graph shown above (Figure 18) depicts the composition of ammonia inside the liquid pool. The ammonia percentage gradually decreases in the pool. However throughout the run very little water actually evaporated to the air. This could be attributed to humidity of the air. For really moist conditions the vapor pressure of water vapor in the air is much greater than the vapor pressure in the pool. However the

moisture will condense and drop back into the pool only if the air temperature equals the dew point temperature at that pressure.

6.3 Sensitivity Analysis

The model will now be tested under different conditions with all the sensitive parameters and suitable discussion will be presented at every stage to justify the working of the model.

6.3.1 Initial Spill Temperature

The temperature of the chemical is probably the most important parameter that could affect the nature of spill and the behavior of the spilled liquid once it begins to evaporate. The model was run at two different initial spill temperatures and the following results were observed. Table 3 shown below summarizes the spill parameters.

Table 3. Cumulative mass of ammonia in air

Weight % of aqueous ammonia	Ground temperature (deg K)	Spill temperature (deg K)	Air velocity (m/sec)	Duration of spill (hours)
28	297	302	5	3

The results for vapor pressure of ammonia and mass vaporization flux of ammonia with time are as follows. The first graph (Figure 19) shows the trend of partial pressure of ammonia in solution with time. The initial partial pressure of ammonia in this case can be compared to the second case with a lower spill temperature. For a spill at 300 K, the initial partial pressure of ammonia is very high and this in turn causes more ammonia to escape from the solution.

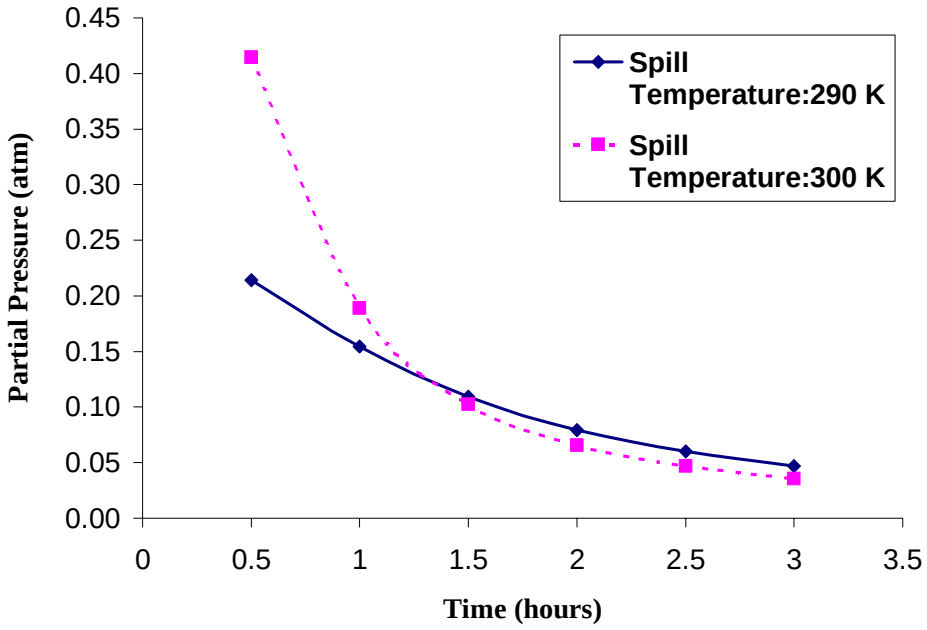

Fig. 19. Partial pressure variation

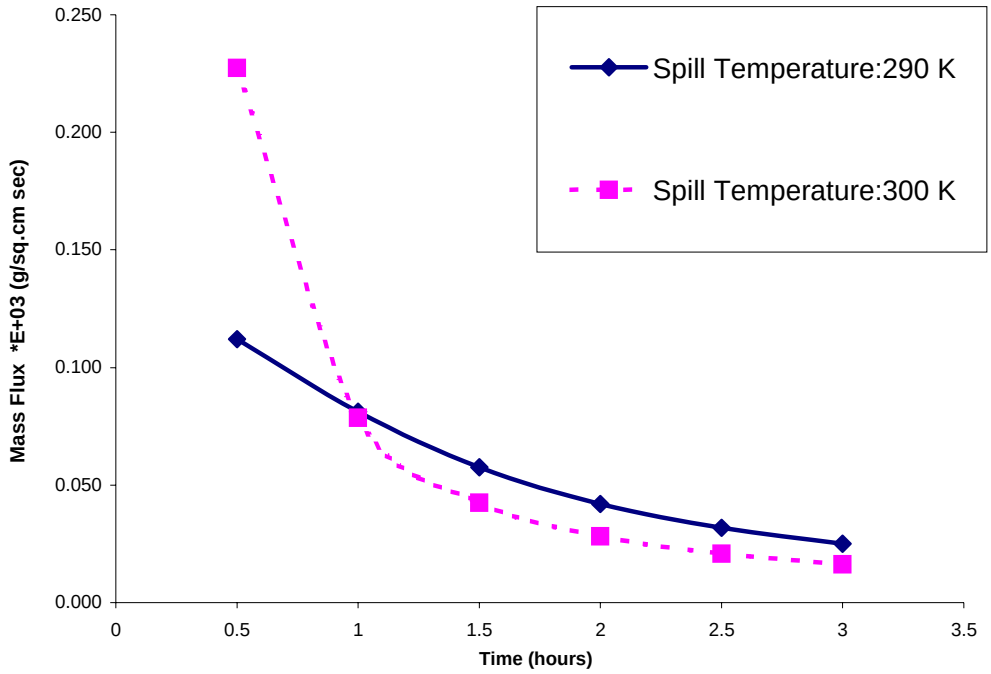

Fig. 20. Mass flux of ammonia in air

However as time progresses, as the ammonia content comes down drastically in the pool in the higher temperature case, the partial pressure drops down drastically (Figure 20). For the lower temperature the mass flux is steady and hence the drop in the partial pressure is also steady.

6.3.2 Wind Speed

Wind speed will play a very important role in the mass transfer equation. The velocity profiles of the lower atmosphere have been studied in detail and it is found that for oil spills, velocity of air above it is very critical in controlling the eddy diffusivity.

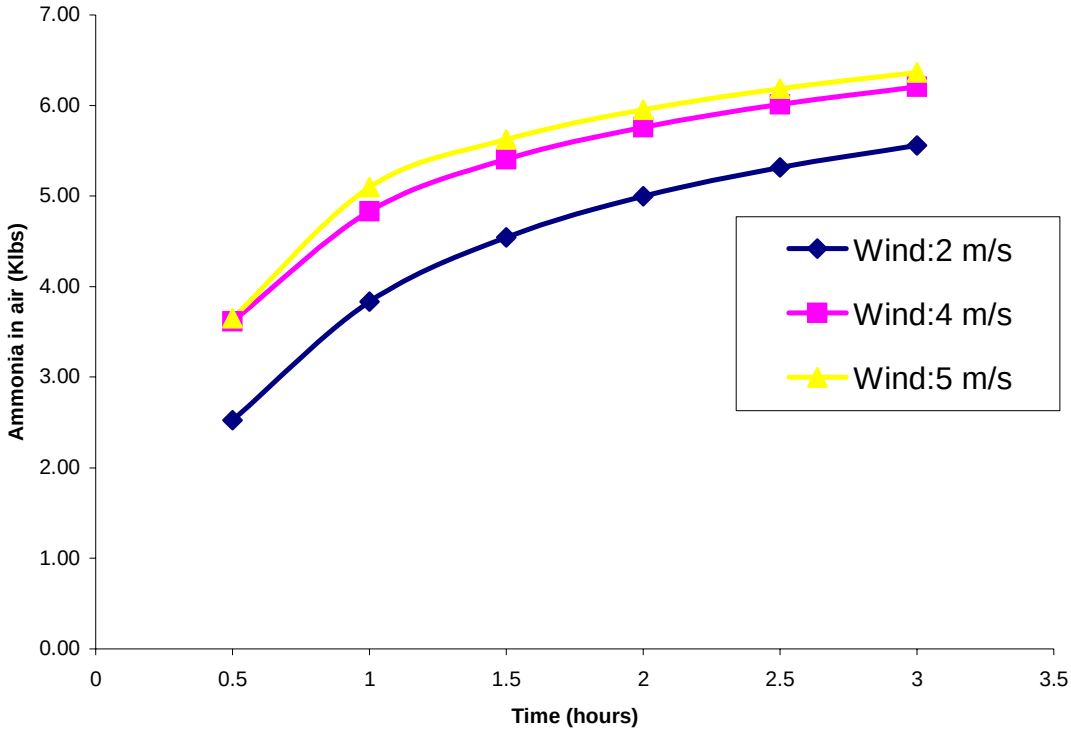

Fig. 21. Effect of wind speed

In this model, Sutton's (Sutton 1953) power law will be applied to the velocity profile. According to this model, velocity is a function of ground roughness and ambient temperature profile .In the graph (Figure 21) shown above, we can see a clear comparison of ammonia entrained at 3 different wind speeds. As the wind speed increases the mass of ammonia entrained also increases. This is consistent with the power law equation 4 for mass transfer.

In fact the wind speed becomes more critical for actual dispersion estimates or toxic endpoint distance. When the toxic plume is being modeled it is observed that as the wind increases the plume becomes longer and narrower. The substance travels faster in air but is also diluted by a larger quantity of air (Crowl and Louvar 2001).

6.3.3 Composition of Chemical

The weight percentage of the toxic chemical determines most of the physical properties and the behavior of the mixture in case of a spill. For aqueous ammonia, if ammonia is present in very small quantities the non-ideal equation used for the partial pressure determination will not be applicable. Moreover the mass transfer correlation developed by Mackay also needs to be modified for very dilute solutions. In the case of concentrated aqueous ammonia solutions the mixture exhibits strong non-ideal properties. The model was run for different composition of aqueous ammonia and the mass flux and temperatures gradient trends were observed.

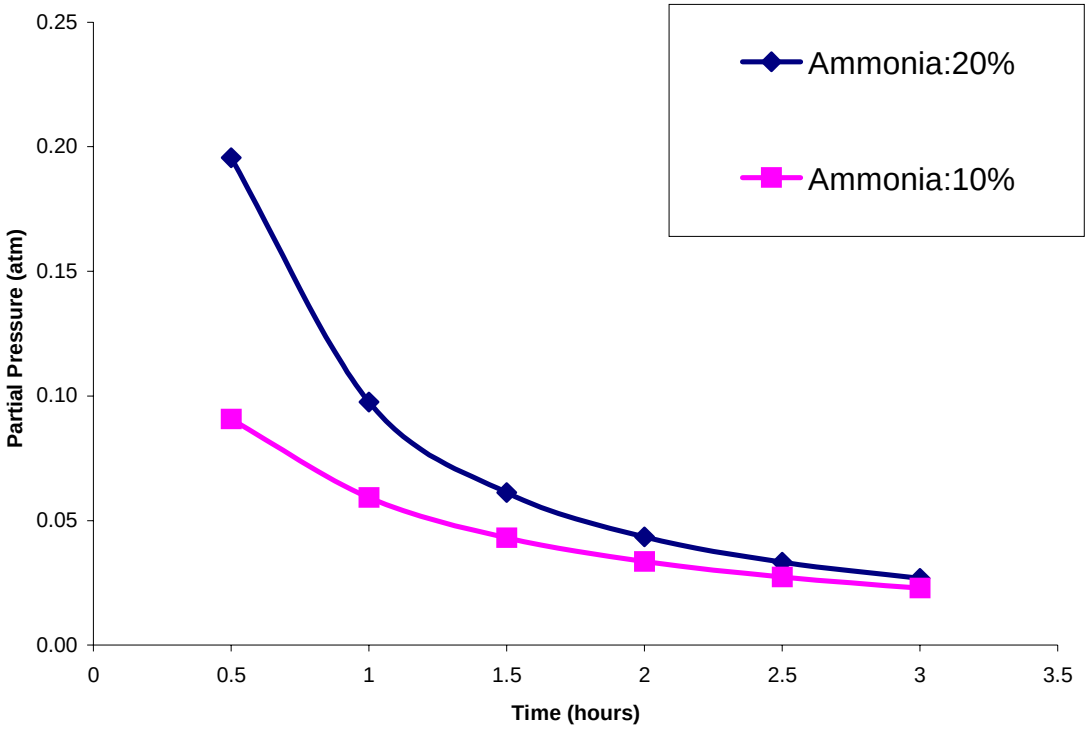

Fig. 22. Effect of composition on partial pressure

The partial pressure graph or Figure 22 shows how partial pressure changes with time for a mixture of 20% ammonia and 10% ammonia. The comparison shows that the partial pressure value for the more concentrated mixture is always higher than that of dilute one. This result is different from the one discussed above for effect of initial spill temperature. This indicates that for aqueous ammonia both energy and mass transfer effects are equally important in the initial phase, however with time mass transfer becomes the driving force for evaporation.

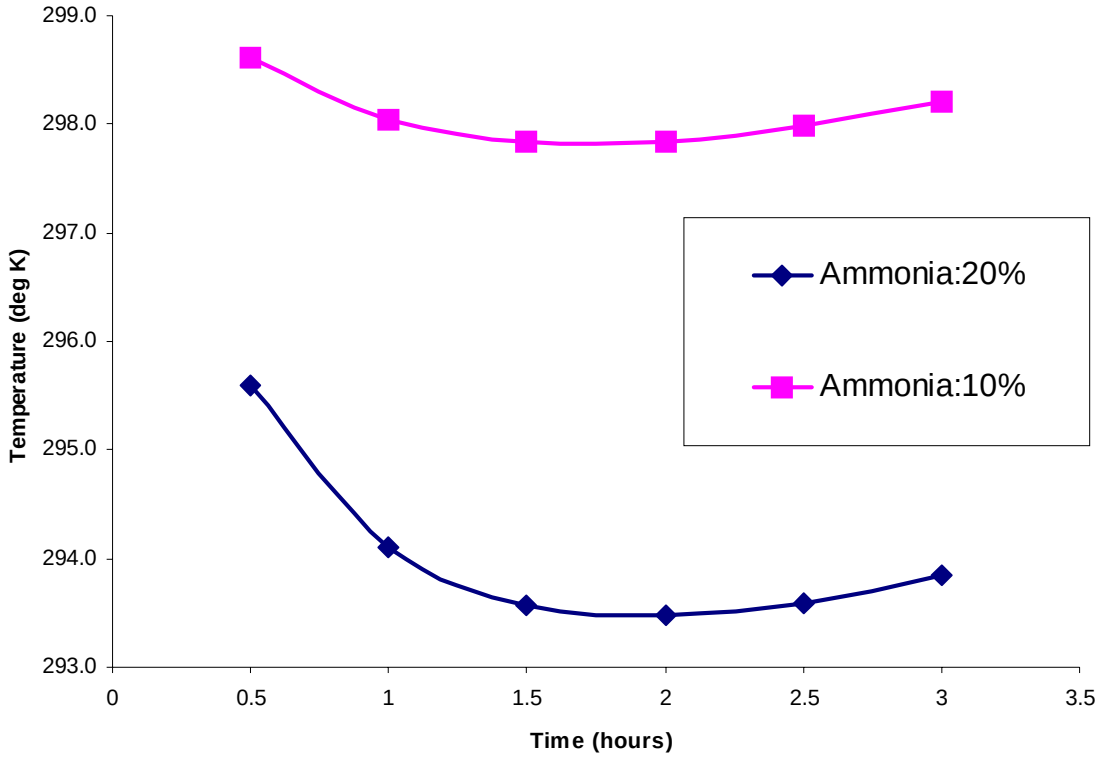

Fig. 23. Effect of composition on surface temperature

The second graph or Figure 23 depicts the effect of composition of temperature of the pool. The evaporative cooling effect is more prominent in the case of a concentrated mixture. This result can be justified by the fact that aqueous ammonia has high enthalpy of vaporization and with increase in concentration these value further increases. Hence the strong influence of non-ideality is again shown at this stage.

6.4 Validation Against Experimental Data

Mikesell et al have carried two experiments for aqueous ammonia on a small scale and the source term has been determined under a specified set of conditions. The general spill conditions for these two experiments are given below in a tabulated form (Table 4). In both these experiments 2240 grams of aqueous ammonia solution was spilled into a pan and allowed to equilibrate for about 2 minutes.

Table 4. Spill conditions for Mikesell et al. data

Experiment	Average Ambient temperature (deg C)	Wind speed (m/s)	Average humidity (%)	Initial spill temperature (deg C)	Weight percentage ammonia (%)	Area of spill (sq cm)
1	24.5	1.59	59	24.5	28.8	522
2	28.9	2.2	68	28.9	28.8	522

At half hour intervals the solution temperature, concentration, air velocity across the front and back of the pan and the average humidity were recorded (Mikessell et al. 1991)**.** The liquid pool evaporation models were run under the same conditions and results (Tables 5 and 6) from both experiments were compared.

6.4.1 Experiment-1

Table 5. Predicted values for experiment 1

Time (hrs)	Experimental data for Ammonia (g) ± 15%	Predicted values for Ammonia (g)					
		Bulk model	Error (%)	Surface model	Error (%)	New model	Error (%)
0.5	190	345	-81	270	-42	228	-20
1.0	240	498	-107	391	-63	339	-41
1.5	300	572	-91	462	-54	405	-35
2.0	350	616	-76	510	-46	449	-28
2.5	400	647	-62	546	-36	482	-20
3.0	420	669	-59	575	-37	507	-20
3.5	450	682	-52	599	-33	529	-17
4.0	490	683	-39	618	-26	547	-11

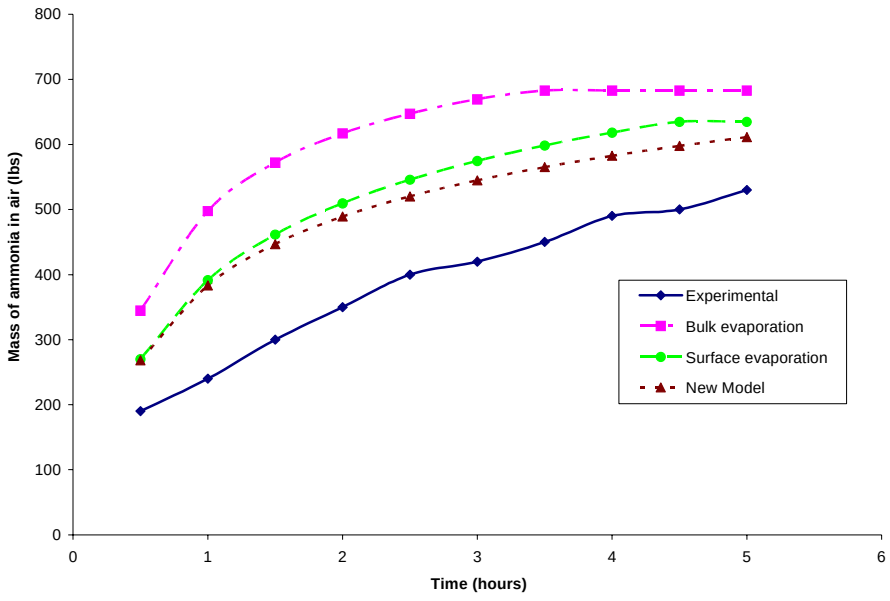

Fig. 24. Experiment 1-Mass of ammonia in air

6.4.2 Experiment-2

Table 6. Predicted values for experiment 2

Time (hrs)	Experimental data for Ammonia (g) ±15%	Predicted values for Ammonia (g)					
		Bulk model	Error (%)	Surface model	Error (%)	New model	Error (%)
0.5	240	377	-57	325	-35	267	-11
1	300	503	-68	454	-51	378	-26
1.5	380	559	-47	518	-36	439	-16
2	420	593	-41	559	-33	480	-14
2.5	470	617	-31	590	-26	510	-9
3	500	634	-27	610	-22	534	-7
3.5	520	648	-25	628	-21	555	-7
4	550	654	-19	645	-17	571	-4

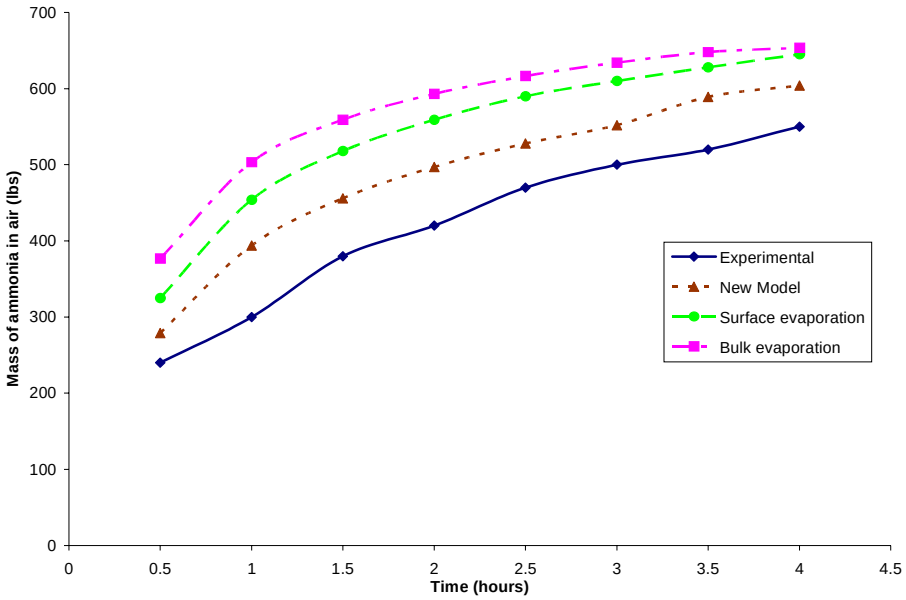

Fig. 25. Experiment 2-Mass of ammonia in air

From the above graphs (Figures 24 and 25) and tabulated values it is evident that the improved liquid pool model predicts the closest values to experimental values and the percentage deviation or error is clearly decreasing. In this case the error is defined as follows:

Error = (Experimental Value – Predicted Value)/Experimental Value

The bulk and surface evaporation models provide over conservative results that might drastically affect the dispersion calculations.

The improved model can now be picked and the validation can be further extended to compare the surface temperature and the composition of the solution at different time instants for both experimental trials.

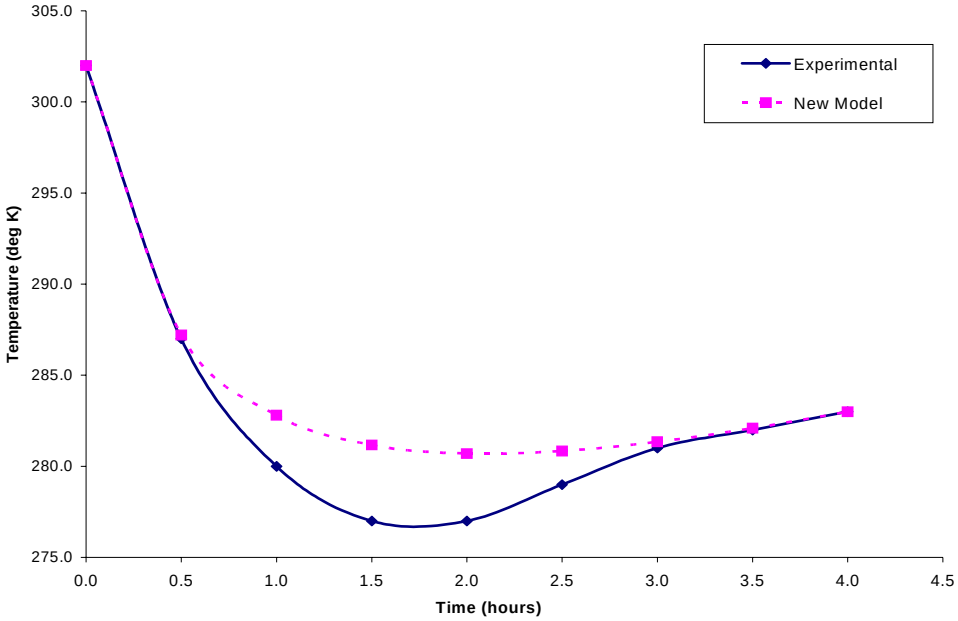

Fig. 26. Experiment 1-Temperature Gradients

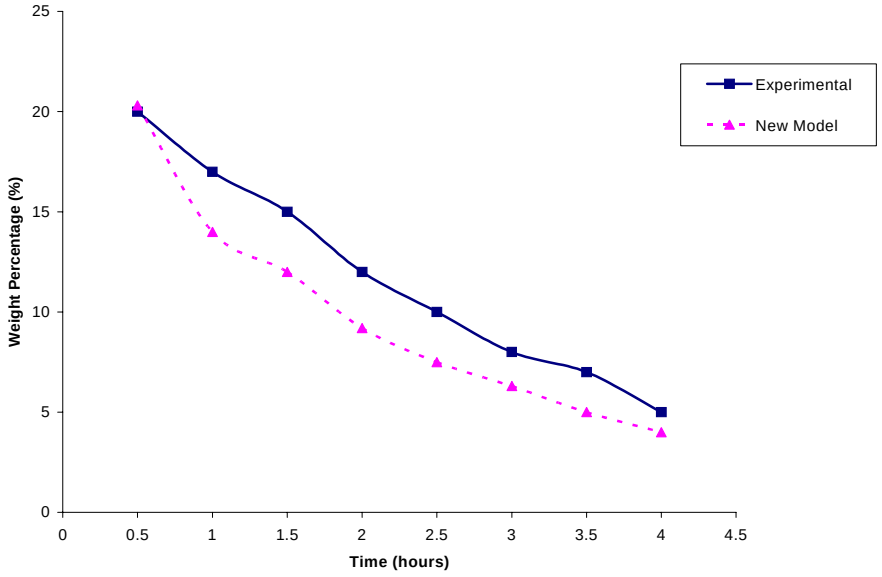

Fig. 27. Experiment 1-Composition of ammonia

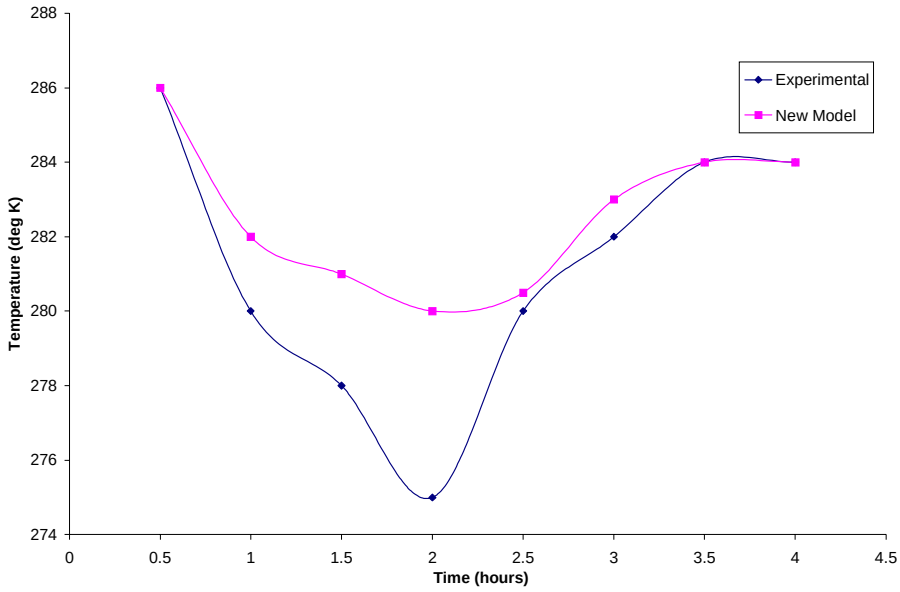

Fig. 28. Experiment 2-Temperature Gradients

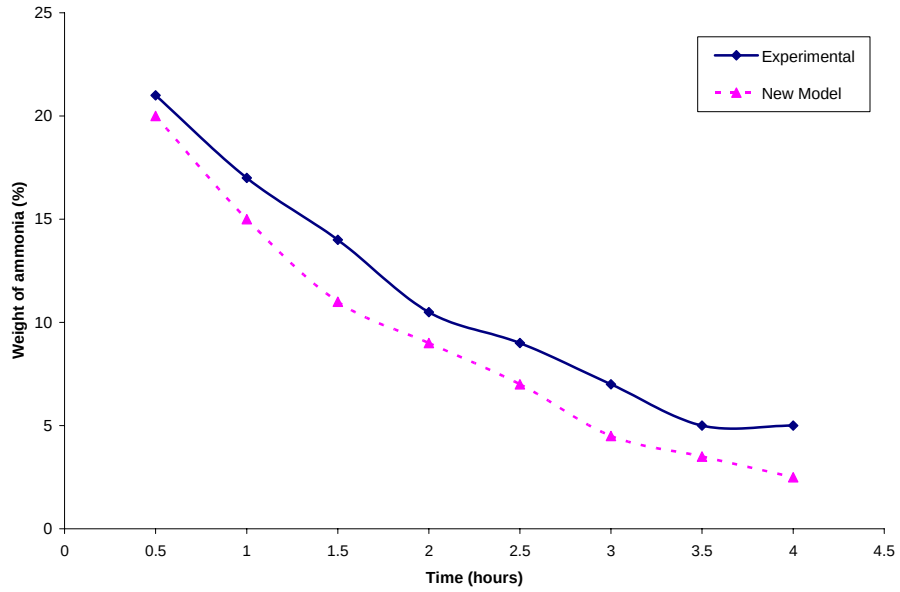

Fig. 29. Experiment 2-Composition of ammonia

The graphs (Figures 26-29) depict the general behavior of the model. The composition of ammonia in the pool and surface temperature were tracked throughout the simulation to make sure that the system is consistent with the model theory.

6.5 Validation for Other Chemicals

The model prediction also needs to be validated for chemicals other than aqueous ammonia to check the generic nature of the model. At this stage two completely different sets of experimental data will be used for this test.

Norman and Dowell (Woodward et al. 2002) conducted indoor and outdoor tests (Table 7). In the indoor test pans were suspended from a tripod and the pure chemical was allowed to evaporate from the pan with an initial depth of 10 cm. The pure chemical, ethanol has been used for this comparison. The chemical was tested for 90 minutes and the source term was recorded. In this particular case, the improved model was run with a single component in the input to compare it with available data.

6.5.1 Test Conditions

Table 7. Test conditions for Norman Dowell data

Ambient temperature (deg C)	Initial spill temperature (deg C)	Air velocity (m/sec)	Relative humidity (%)	Initial pool depth (cm)	Area of pan (sq.cm)
20	20	0.1-1	35	10	113

6.5.2 Ethanol Data Comparison

Table 8. Predicted values for ethanol

Time (minutes)	Experimental data for Ethanol (g/sq cm sec) *1E-04 ±10%	Predicted values for Ethanol (g/sq cm.sec) *1E-04			
		Model	Error (%)	ALOHA	Error (%)
10	0.48	0.51	-6.7	0.63	-30
20	0.42	0.51	-22	0.58	-38
30	0.40	0.5	-28	0.58	-44
40	0.38	0.5	-35	0.56	-47
50	0.36	0.5	-42	0.54	-50
60	0.36	0.49	-39	0.52	-44

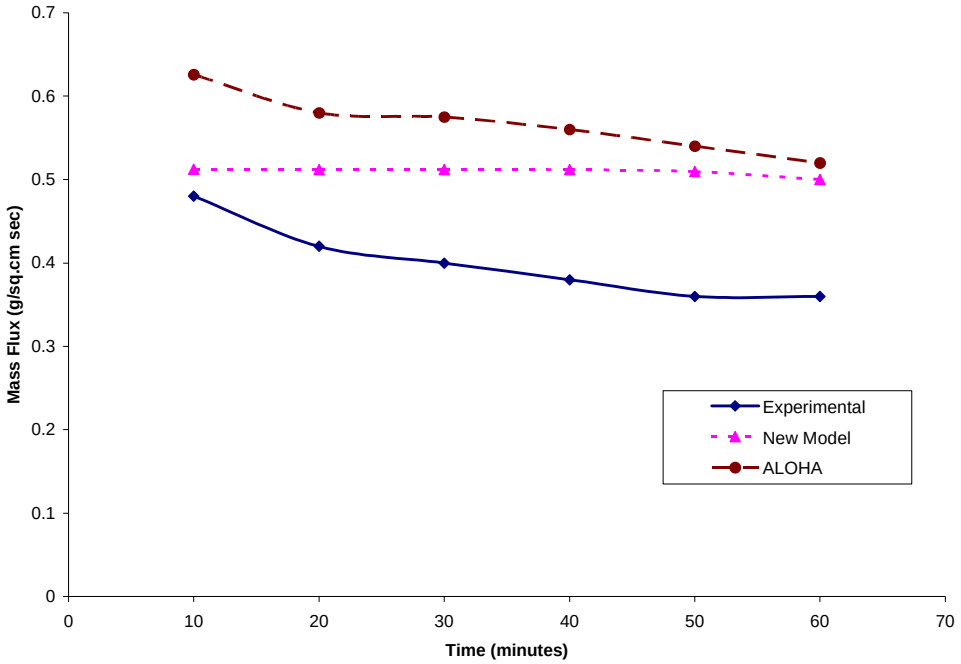

Fig. 30. Mass flux of ethanol

On comparing the experimental values (Table 8 and Figure 30) with the improved model and ALOHA, it is very clear that ALOHA over predicts the values with an average deviation of 42% .The new model predicts values much closer to the experimental data.

6.5.3 Propylene Data Comparison

Table 9. Predicted values for propylene

Time (minutes)	**Experimental data for Propylene (g/sq cm sec) *1E-04 ±10%**	**Predicted values for Propylene (g/sq cm.sec) *1E-04**			
		Model	**Deviation (%)**	**ALOHA**	**Deviation (%)**
10	2.6	2.72	-4.6	4	-54
20	2.6	2.72	-4.6	3.7	-42
30	2.6	2.72	-4.6	3.7	-40
40	2.6	2.72	-4.6	3.5	-35
50	2.6	2.72	-4.6	3.5	-33
60	2.6	2.72	-4.6	3.5	-33

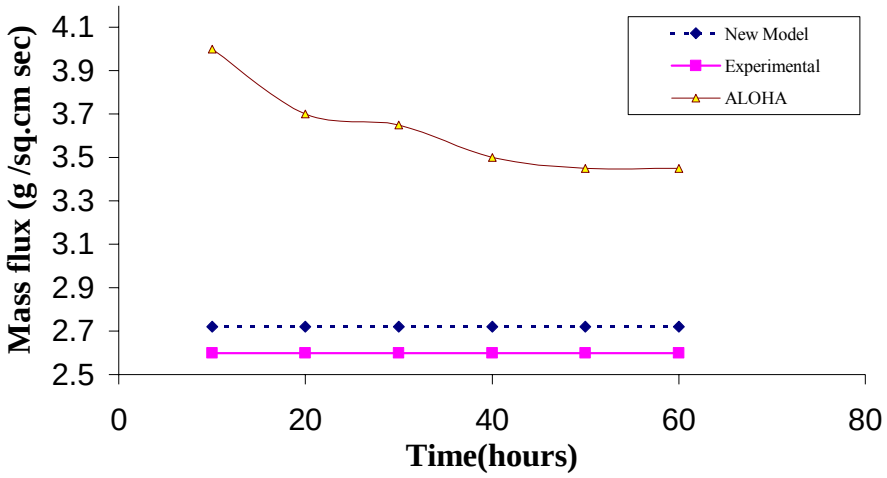

Fig 31. Mass flux of dichloromethane

The experimental values are compared with the improved model and ALOHA (Table 9 and Figure 31), and again it is very clear that ALOHA over predicts the values with an average deviation of 39%. The model predicts values much closer to the experimental data.

At this stage the model is predicting the mass flux values with good accuracy. However the validation of aqueous ammonia still shows that the average error can be further reduced to predict values closer to the actual ones. The model's prediction under more realistic conditions depends on the atmospheric conditions during the spill and few important points in this context also need to be addressed. Moreover some of the limitations of the model will also be listed in the following paragraphs.

6.6 Applicability of the Model Under Different Meteorological Conditions

The source term model developed in this work predicts emission rates much closer to experimental data and hence reduced the deviation from actual values. These source term values are in turn fed into a dispersion model to estimate the distance to the toxic endpoint. The meteorological conditions might sometimes have a great effect on the

model predictions and the error associated with the dispersion model predictions might just not be from the source term model alone. A few key meteorological parameters that need to be analyzed are ambient temperature, wind speed, and relative humidity and each of these parameters will affect the source term and the dispersion model used. The applicability of our model under extreme conditions will be discussed with reference to the extreme weather conditions in different parts of the U.S.

Table 10. Meteorological conditions around the U.S.

Parameters	**Houston, Texas**	**Midland, Michigan**	**Jersey City, New Jersey**	**Los Angeles, California**
Ambient temperature (deg F)	93.5	16.1	27.5	81.1
Relative humidity (%)	92	82	55	54
Wind speed (mph)	6.2	11.1	11.4	6.6

Table 10 presented above gives us the extreme weather conditions picked from the National weather service data.

Ambient Temperature: The model takes into account the ambient temperature conditions in the heat and mass transfer calculations. For aqueous ammonia, it is usually stored at ambient temperature and for all the above-mentioned temperatures; it will not have any significant flashing effects. Hence the model should be able to estimate the chemical release rate with good accuracy.

Relative Humidity: In this case for extreme conditions like Houston with more than 90% humidity, the vapor pressure of water vapor can be greater than the partial pressure of water at many stages during the evaporation and this could cause the condensation of some water molecules back into the pool. This could affect the performance of the model to some extent, as the model does not account for mass transfer into the pool. For places like Los Angeles, with very mild climatic variations throughout the year, the humidity never exceeds 60% and the model will work perfectly fine under these conditions.

Wind Speed: The model uses the Sutton's power law equation. But at very high speeds it has been proved with experiments that an empirical correlation with a logarithmic profile for wind velocity is more suitable. The high wind speeds like that in Midland could result in greater turbulence and more mixing in the air. The vapor cloud in this case cannot actually be treated like a cylindrical vapor cloud and the. Moreover at high wind speeds the plume becomes narrower and longer.

6.7 Limitations of the Model

- The effect of spreading is neglected and can be important for some highly viscous fluids.
- The ground surface is assumed to be dry and presence of water would cause ammonia to react with water.
- The ground surface is assumed to be at a constant temperature with heat flux depending only on the pool temperature.
- The mixing of the pool contents is not considered explicitly and this effect could be important for some cryogenic fluids.

CHAPTER VII

MODELING SOFTWARE

This chapter is intended to help the user to get an overview of the code written to develop this model. The non- linear and other differential equations handled in the model need to be solved systematically and efficiently. The Matlab software has a lot of built in functions that can be used to solve these mathematical equations.

MATLAB is a high-level technical computing language that provides tools for algorithm development, data visualization, data analysis, and numerical computation. MATLAB can be used to solve technical computing problems faster than with traditional programming languages, such as C, C++, and FORTRAN. Some of the key features of this software that helped develop this dynamic model are

- Interactive tools for complex design problems.
- Mathematical functions for linear algebra, partial differential equation, statistics, optimization, and numerical integration
- Graphics functions for representing data in multi-dimensions.
- Functions for integrating MATLAB based algorithms with external applications, such as FORTRAN, Microsoft word, and Microsoft Excel.

7.1 Programming and Key Functions Used

The Matlab code was written to estimate the vaporization rate of the chemical and also to keep track of the various important parameters involve din modeling. The temperature inside the pool was solved using some PDE solvers. Some of the important functions (MathWorks 2004) used in this code are:

- **SOLVE** - Symbolic solution of algebraic equations

  A typical example of a SOLVE function is shown below

  SOLVE ('eqn1','eqn2'...'eqnN','var1, var2...varN')

  The 'eqns' are symbolic expressions or strings specifying equations. The 'vars' are symbolic variables or strings specifying the unknown variables. SOLVE seeks zeros of the expressions or solutions of the equations. If no analytical solution is found and the number of equations equals the number of dependent variables, a numeric solution is attempted.

- **INLINE** - Object

  The command 'INLINE (EXPR)' constructs an inline function object from the MATLAB expression contained in the string EXPR. The input arguments are automatically determined by searching EXPR for variable names. This function was used to feed the input to dynamic partial pressure equation.

- **PLOT** - Linear plot

  'PLOT (X, Y)' plots vector Y versus vector X. If X or Y is a matrix, then the vector is plotted versus the rows or columns of the matrix, whichever line up. If X is a scalar and Y is a vector, length (Y) disconnected points are plotted. The plots to show the time dependency of vapor pressure, mass flux are done using this function.

- **BVP4C**

  This function is used to solve boundary value problems for ODEs by collocation. SOL = BVP4C (ODEFUN, BCFUN, SOLINIT) integrates a system of ordinary differential equations of the form y' = f (x, y) on the interval [a, b], subject to general

two-point boundary conditions of the form bc (y (a), y (b)) = 0. ODEFUN is a function of two arguments: a scalar X and a vector Y. ODEFUN (X, Y) must return a column vector representing f (x, y). In this ODE solver BCFUN represents the boundary condition for the differential equation. SOLINIT specifies the initial condition for the same equations.

7.2 Algorithm

A source code was written in **MATLAB 6.5** to calculate the vaporization rate at different time instants after a chemical spill and the cumulative mass for each component. The following algorithm will give a brief overview of the code.

Start

Step-1:

- The input and other program variables are declared and initialized.
- The variables used in the loops are initialized to zero at the beginning.
- The actual input will include initial concentration, temperature, area, pool mass and some physical properties.
- All the other physical properties are also loaded into the Matlab file.

Step-2:

- The iteration (time loop) for calculating all those properties that changes with time starts here.
- Some of the average properties are defined, including vapor pressure.

Step-3:

- Iteration for tracking all the components in solution begins here

Step-4:

- The mass and heat transfer equations are defined here and an initial solution is determined.

Step-5:

- The temperature and the mass flux terms are interdependent and need to be solved in a non-linear fashion.
- The routines *newbvp*, *twobc* and *twode* are separate functions that are called in this main program.

Step-6:

The feedback is then given to start of the time loop to recalculate the properties.

Step-7:

- In this step all output plots are generated using the 2-d or 3-d plot function to display the time varying mass flux and other key results.

End

The input to the code can be entered manually or using an interactive software like Microsoft Excel. The main code that was written in MATLAB is presented below (Figure 32).

GLOBALIZATION AND INTIALIZATION BEGINS

```
global tt; %% Time variable used for pseudo equilibrium   calculations.
global array; %% variable used for passing values from newbvp to main program ( Tbulk
values)
array=zeros(100,20); %% The array initial values are set to zero
global TIME;
global x ;  %% Variable is used for moisture check.
global m1;  %% mass of vaporization of ammonia
global j;   %% Main looping variable
global m2; %5 mass of vaporization of water
xx=linspace(1,5,5);  %%  Depth is assumed to be 5 cm.
timetime=linspace(1,16000,20);
global Tb; %%  Bulk temperature variable
global vijay; %% surface temperature variable.
```

Fig. 32. Matlab Code

```
global check;
global condensationtemp; %% used in routine “cloud” as condensation temperature
```

```
global pnh3final; %% Partial pressure of ammonia
global ph20final; %% Partial pressure of water
global kk;   %%
global wnh3; %% weight fraction of ammonia
global check2;
global densitykg; % % Density of  cloud in kg/m3
global yvnh3;%% mole fraction of ammonia in vapor
global yvh2o;
global areanew;
index=1;
Mpool=10^7; %% Intial spill mass
mixturedensity=.896;
userarea=(Mpool/mixturedensity)/4.2 ;
areanew= userarea;
matrixrv=300;  %%
Ts1=302;% %Surface temperature, can be user input.
Tb=302; %% Bulk temperature, can be user input.
Tg=297;  % %Ground temperature, can be user input.
wnh3= 28.80;%% Weight fraction of chemical
deltasol=302;
h2evap=0;
nh3evap=0;
p=1;
tt=600;
flag=0;
```

GLOBALIZATION AND INTAILIZATION ENDS

MAIN BODY OF CODE BEGINS

```
for j=1:18  %% Main Time Loop begins here
TIME=j;
Tbav=373.2-2.663*wnh3+.0133*wnh3^2;
Cpav=4.2-.006*wnh3+.000191*(wnh3)^2;
massammoniacumu(1)=0;
pnh3=inline('exp(17.17-4294/Ts+(.137*wnh3)-
(.00347*wnh3^2)+(23.01*wnh3/Ts))');%% vapor pressure of ammonia
ph20=inline('exp(18.37-4552/Ts+(.1477*wnh3)-(.00081*wnh3^2)-(43.53*wnh3/Ts))');
%%vapor pressure of water
for h= 1:10 %%Loop to check for convergence.
ph=ph20(Ts1,wnh3)/760;
```

Fig. 32. Continued

```
pn=pnh3(Ts1,wnh3)/760;
pntemp(j)=double(pn);

aa(j)=double(ph);
bb(j)=double(pn);
rv=double(ph)
x=double(ph-.0167)% flag to check humidity difference.
Da(1)=0.2161;
Da(2)=0.2164;
viscosityair=.158;
Sc(1)= viscosityair/Da(1);
Sc(2)=viscosityair/Da(2);
MW(1)=18;
MW(2)=17;
R=82.05;
u= 5*3600;
Length=((areanew*4/3.14)^.5)/100;
km(1)=(2.7*10^-2*(u^.78)*(Length^-.11)*(Sc(1)^-.67))/36;
km(2)=(2.7*10^-2*(u^.78)*(Length^-.11)*(Sc(2)^-.67))/36;
if x>0
flag=flag+1;
mm=double(km(1)*MW(1)*(ph-0.0167)/R/Ts1+km(2)*MW(2)*(pn-0)/R/Ts1);
mm= double(1.516*10^(-1)*(pn-0)/Ts1)+double(1.645*10^(-1)*(ph-.0167)/Ts1)
mass(j)=double(mm);
else
mm= double((km(2)*MW(2)*(pn-0)/R/Ts1));
mass(j)=double(mm);
end
syms Ts
S=(2.079*10^-6*(302-Ts)+3.17*10^-2*(Tb-Ts)+(9.81*10^-3)-deltasol*mm);
k=solve(S,Ts);
Ts1=k;
m1=double(km(2)*MW(2)*(pn-0)/R/Ts1);
m2=1.58*10^-3*(ph-.0312)/Ts1;
end   %% This end corresponds to the 'h' loop.
global Tsurface
Tsurface=double(Ts1) %%Tsurface is just copied to  a new variable
Tsurface
ts1(j)=Tsurface;
weightnh3(j)=wnh3;
newbvp %  New bvp function call for  differential equation solution
matrixrv(j)=vijay;
for loop=1:5
newarray(TIME,loop)=array(TIME,loop);
end
tb1(j)=Tb;
```

Fig. 32. Continued

```
Mntemp=m1*areanew*tt; %% Mass of  ammonia that is evaporated
nh3evap=nh3evap+Mntemp;
m2=double(km(1)*MW(1)*(ph-0.0167)/R/Ts1);%  Cumulative mass
massammonia1(j)=m1;
masswater2(j)=m2;
massammoniacumu(j+1)=m1*areanew*tt+massammoniacumu(j);
if x>0
m2=double(km(1)*MW(1)*(ph-0.0167)/R/Ts1) %% RV needs to check these values and
replace with generic terms
Mhtemp=m2*areanew*tt;
h2evap=h2evap+Mhtemp;
xn=(Mntemp/17)/((Mntemp/17)+(Mhtemp/18));
xh=1-xn;
deltanh3=5562*((1-Tsurface/385)/.377)^.38;
deltah20=10598*((1-Tsurface/647)/.423)^.38;
deltasol=double(deltanh3*xn/17+deltah20*xh/17);
Mpoolnew=Mpool-(Mntemp+Mhtemp);
wnh3=100*((wnh3/100*Mpool)-Mntemp)/Mpoolnew
Mpool=Mpoolnew;
massammonia1(j)=m1;
masswater2(j)=m2;
time(j)=tt*j/60;
if wnh3<0
   break;
end
else
   time(j)=tt*j/60;
   deltanh3=327.22*((1-Tsurface/385)/.43)^.38;
   deltasol=double(deltanh3);
   Mpoolnew=Mpool-(Mntemp);
      wnh3=100*((wnh3/100*Mpool)-Mntemp)/Mpoolnew
Mpool=Mpoolnew;
end
weightpercent(j)=wnh3;
cloudhouston
temparray(index)=densitykg;
tempcloud(index)=kk;
tempyvnh3(index)=yvnh3;
tempyvh20(index)=yvh2o;
tempcheck(index)=check2;
tempcondensationtemp(index)=condensationtemp;
index=index+1;
end
```

Fig. 32. Continued

MAIN BODY OF CODE ENDS

PLOTS & FIGURES

```
for nb= 1:j
   masscumuammonia(nb)=massammoniacumu(nb+1);
end
dlmwrite('alpha.xls',temparray,'\t',0,0)
plot(time,massammonia1,'-.b*','Linewidth',2)
ylabel(' mass flux ()')
xlabel('Time in Minutes')
plot(time,tempcloud)
ylabel(' condensation temp (K)')
xlabel('Time in Minutes')
figure;
plot(time,temparray)
ylabel(' density of air (g/cm3)')
xlabel('Time in Minutes')
SURF(xx,time,newarray)
```

END

Fig. 32. Continued

CHAPTER VIII

CONCLUSION AND FUTURE WORK

The Selective Catalytic Reduction (SCR) technology is now being applied to a wide variety of emission systems and has in turn the increased demand of aqueous ammonia. All the facilities using aqueous ammonia need to submit their updated Risk Management Plan to the EPA. However most of them are still using the anhydrous ammonia source term models to model the release scenario for aqueous ammonia. Appendix 1 discusses the difference in behavior of the dense gas clouds for both these compounds and justifies the use of different source term models.

This new improved model is capable of handling multi-component non- ideal mixtures. The relevant mass and heat transfer mechanisms have been incorporated into the model with particular emphasis on the temperature gradients within the pool. The transient model was built in several stages and improved at every stage to predict source term values with more accuracy. The model has also been validated extensively with experimental data and is found to perform well even with pure chemicals .The comparison of the model with publicly available models like ALOHA further proves its reliability.

With improving dispersion modeling techniques, the need for more realistic source term modeling is growing. The performance of the source term models clearly affects the dispersion model in predicting downwind concentrations. Hence this robust, user-friendly model will help process engineers predict the consequences from chemical releases with more confidence.

There is a reasonably good potential to improve this model further with lesser assumptions by using a slightly different approach. In this case the liquid pool can be broken down into small meshes and the principle of Rayleigh Benard convection be used

to model the system. This work will help us predict the source term from all points in the pool with more accuracy and feed this as an input to Computational fluid dynamic (CFD) models. A more detailed discussion of this idea has been done in Appendix B and requires further work to develop the idea into a fully working dynamic model.

REFERENCES

AWS. (1978). "Calculation of toxic corridors." *AWS Pamphlet*, Air Weather Service, 105, 57.

Byron, R. B., Stewart, W. E., and Lightfoot, E. N. (2000). *Transport Phenomena*, John Wiley and Sons, New York.

Cavanaugh, T. A., Siegell, J. H., and Steinberg, K. W. (1994). "Simulation of vapor emissions from liquid spills." *Journal of Hazardous Materials*, 38(1), 41-63.

Cormack, D. E., Leal, L. G., and Imberger, J. (1974). "Natural convection in a shallow cavity with differentially heated end walls .1. Asymptotic theory." *Journal of Fluid Mechanics*, 65(8), 209-229.

Crowl, D. A., and Louvar, J. F. (2001). *Chemical Process Safety*, Prentice Hall PTR, Upper Saddle River, New Jersey.

EPA. (1998). "General guidance for risk management programs (40 CFR Part 68)." U.S. Environmental Protection Agency, Washington, District of Columbia.

EPA. (2004). "Changes to chemical accident prevention rule in 2004." Chemical Emergency Preparedness and Prevention Office, Chemical Emergency Preparedness and Prevention Office, Washington, District of Columbia.

Fleischer, M. T. (1980). "SPILLS-an evaporation/air dispersion model for chemical spills on land." Shell Development Company, Houston, Texas.

Frie, J. L., Page, G. A., and Buckland, A. C. (1992). "Improved evaporation model for spills of multicomponent non-ideal liquids." *Heat Transfer, AIChE Symposium Series*, 88, 344-349.

GEC. (1999). "NOx removal system by SCR process." Global Environment Center Foundation, Available at http://nett21.gec.jp/CTT_DATA/AIR/AIR_3/html/Air-115.html

Hanna, S. R., and Drivas, P. J. (1987). *Guidelines for Use of Vapor Cloud Dispersion Models*, Center for Chemical Process Safety, New York.

Ille, G., and Springer, C. (1978). "The evaporation and dispersion of hydrazine propellants from ground spills." *CEEDO 712-78-30*, Civil and Environmental Engineering Development Office, Asheville, North Carolina.

Kawamura, P. I., and Mackay, D. (1987). "The evaporation of volatile liquids." *Journal of Hazardous Materials*, 15(3), 343-364.

Klosse, K., and Ullersma, P. (1973). "Convection in a chemical vapor transport process." *Journal of Crystal Growth*, 18(2), 167-174.

Kunkel, B. A. (1983). "A comparison of evaporative source strength models for toxic chemical spills." Atmospheric Sciences Division, Air Force Geophysics Laboratory, Hanscom, Massachusetts.

Mackay, D., and Matsugu, R. S. (1973). "Evaporation rates of liquid hydrocarbon spills on land and water." *Canadian Journal of Chemical Engineering*, 51(4), 434-439.

Mary, E., Jones, R., and Overstreet, R. (1993). "Modeling hydrochloric acid evaporation in ALOHA." National Oceanic and Atmospheric Administration, Seattle.

MathWorks. (2004). "Matlab." The Mathworks, Inc., Available at http://www.mathworks.com/

McCay, D. P. F., Isaji, T. (2003). "Evaluation of the consequences of chemical spills using modeling: chemicals used in deepwater oil and gas operations." *Environmental Modeling & Software*, 19(7-8), 629-644.

Mikessell, J. L., Buckland, A. C., Diaz, V., and Kives, J. J. "Evaporation of contained spills of multicomponent non ideal solutions." American Cyanamid, Inc., Wayne, New Jersey.

OSHA. (1992) "Permissible exposure limits." Occupational Safety and Health Association, Washington, District of Columbia.

Pritchard, S. G., DiFrancesco, C. E., and Von Alten, T. R. (1995). "SCR catalyst performance under severe operation conditions." CORMTECH, Inc., Durham, North Carolina.

Raj, P. K. (1980). "Emission from liquid pools." Arthur D Little, Boston, Massachusetts.

Raj, P. K. (1981). "Models for cryogenic liquid spill behavior on land and water." *Journal of Hazardous Materials*, 5(1-2), 111-130.

Reid, R., and Sherwood, T. (1966). *Properties of Gases and Liquids*, McGraw-Hill Inc., New York.

Shaw, P., and Briscoe, F. (1978). "Vaporization of spills of hazardous liquids on land and water." *SRD R 100*, United Kingdom Atomic Energy Authority Safety and Reliability Directorate, Abingdon, Oxon.

Studer, D. W., Cooper, B. A., and Doelp, L. C. (1988). "Vaporization and dispersion modeling of contained refrigerated liquid spills." *Plants/Operations Progress (Process Safety Progress)*, 7(2), 127-135.

Sutton, O. G. (1953). *Micrometeorology*, McGraw-Hill, New York.

Woodward, J. L., Krishna , K., and Bagais, A. (2002). "Validation and extension of pool evaporation and flashing blowdown models." *International Conference and Workshop on Risk and Reliability*, Jacksonville, Florida, 1-15.

APPENDIX A

ESTIMATION OF CLOUD DENSITY

A.1 Introduction

The modeling of ammonia release in anhydrous form and aqueous form needs to be treated separately. However in many cases the models applied to anhydrous ammonia is also used to model aqueous ammonia releases. The difference in modeling techniques can be discussed with respect to the vapor cloud behavior. The vapor cloud resulting from ammonia release will differ in its density depending on the amount and phase of ammonia actually being transferred into air. The denser vapor cloud will slump more easily to the ground compared to the buoyant cloud and this has a direct effect on the toxic endpoint calculation. In most cases the dense cloud will become slowly buoyant as it mixes with the huge volume of air over time. The density and temperature of the cloud in the first few minutes after the release will help us check the nature of cloud and the applicability of the model.

A.1.1 Properties of Ammonia- Water Vapor Mixture in Air

The ammonia and water vapor evaporate from the pool with time and this will affect the physical properties of the vapor cloud. The major assumption in this discussion is that air above the pool is maintained at 1 atmosphere pressure and that the initial and final clouds are at thermal equilibrium. The thermodynamics of the ammonia –water vapor mixture in air needs to be studied in detail to estimate its density with time. In a practical scenario, the air above the pool will be humid and this factor needs to be accounted while performing these calculations. The physical state of the final cloud will be systematically determined by solving the mass and energy balance equations of the cloud mixture.

A.1.2 Stepwise Estimation of Final Cloud Conditions

The first step in these calculations will be the mass balance for the initial and final cloud.

Though it's a mass balance equation, moles will be used throughout the expression.

A.1.2.1 Mass Balance

$$\left[N_k^{vap} + N_k^{liq}\right]_{initial} = \left[N_k^{vap} + N_k^{liq}\right]_{final} \quad (17)$$

where ,

N_k^{vap} = Moles of component 'k' in the vapor phase.

N_k^{liq} = Moles of component 'k' in the liquid phase

In this case the initial condition is when no chemical has evaporated into the cloud and the final condition is fixed based on the time at which measurements are required.
In the first stage the cloud is assumed to be made up of fully vapor. This assumption will make the ' N_k^{liq} ' term zero at the initial and final stages.

A.1.2.2 Energy Balance

In this part of the problem, an ammonia- water vapor cloud above the liquid pool is considered. Further the cloud is assumed to be homogeneous. An enthalpy balance for each of the constituents entering the cloud is performed assuming pseudo equilibrium for a given small amount of time Δt. This equation will also take into account the initial water vapor present in the cloud, hence the final temperature of the cloud at every time instant is noted.

$$\sum\left(N_k^{vap}h_k^{vap} + N_k^{liq}h_k^{liq}\right)_{final} + \sum\left(N_k^{liq}\Delta H_{mix}\right)_{final} = \sum\left(N_k^{vap}h_k^{vap} + N_k^{liq}h_k^{liq}\right)_{initial} + \sum\left(N_k^{liq}\Delta H_{mix}\right)_{initial}$$

(18)

where,

h_k^{vap} = Vapor Phase enthalpy

h_k^{liq} = Liquid Phase enthalpy

ΔH_{mix} = Enthalpy of mixing of ammonia and water per unit quantity of final solution.

The mass transfer and the heat transfer equations can be solved simultaneously for the temperature of the cloud and using this temperature the density of the mixture can be found out under ideal conditions.

If the temperature exceeds the dew point measurement at any time instant, then the respective chemical will condense out of the mixture and there is a great possibility of forming a dense gas mixture. However if there is no condensation, the full vapor cloud mixture will be less dense and has the potential to lift off quickly.

A subroutine was written in Matlab to calculate the final density of the cloud and this was called in the main code to plot a graph of density at different times. The following section will show the results at two different compositions of aqueous ammonia.

A.2 Calculation of Cloud Density

The two important factors that will decide the density of the mixture will be the composition of aqueous ammonia and the cloud volume used in calculations. In this problem the cloud formation step is used to define its initial shape. At release time, the cloud is assumed to take the shape of a vertical gas cylinder characterised by its radius "R" and its height "H". The main assumption is that its mass density ‘ρ’ is within the whole cloud. The main input of this step is the cloud volume. It can be given either by

the volume or the cloud initial mass and its surface area at the ground, where 'ρ' is the initial mass density of the cloud. In our case we can consider the volume of cloud just above the diked containment area. Now the results will show the effect of both the ammonia concentration and cloud volume.

Test Conditions

Table 11. Test conditions for density validation

Ground temperature (deg K)	**Ambient temperature (deg K)**	**Spill temperature (kg)**	**Air velocity (m/sec)**	**Relative Humidity (%)**	**Density of moist air (g/cu.cm)**	**Duration of spill (hours)**
297	303	293	2	50	1.09	3

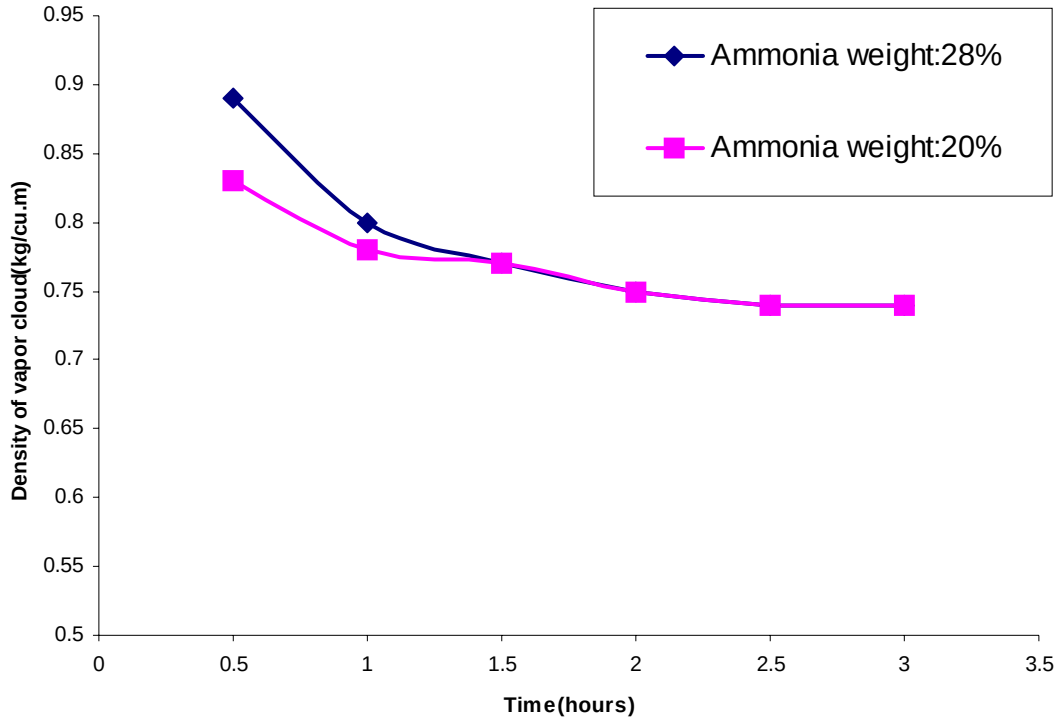

Fig. 33. Density of vapor cloud

The spill parameters used in this run are presented in Table 11 .The density of the cloud in most cases was found not to exceed the density of the moist air. As the ammonia solution gets weaker the density of vapor cloud goes down further justifying the fact that lesser ammonia goes up into the air. This is clearly shown in the above figure. (Figure 33)

Further the cloud volumes were changed and the density of the cloud changed as follows. The cloud volume is estimated based on a ratio between the pool volume and the air above it and this ratio is called the cloud volume factor .So a cloud volume factor of '5' means that the air above the pool is five times the pool volume. As this factor increases the dilution of the chemical in air should also increase.

Table 12. Cloud density at different time instants

Cloud Volume Factor	**Cloud density (kg/cu.m)**		
	30 (mins)	60(mins)	90(mins)
5	0.89	0.80	0.77
10	0.80	0.76	0.74
20	0.75	0.74	0.74

It can be clearly seen from the above tabular column (Table 12) that the cloud becomes less dense due to rapid mixing with the air above it. On the whole for most aqueous ammonia spills the density of the vapor cloud stays below that of air density and this depicts the need for different modeling technique for aqueous ammonia.

APPENDIX B

CONVECTION DRIVEN EVAPORATION METHOD

The transient model described above accounted for the temperature variation along the depth but treats the pool of liquid as a stagnant layer of fluid .In this case conduction is assumed to be the controlling factor. This assumption holds good for most of the liquids modeled under EPA's worst-case release scenario. However for cryogenic liquids, it is believed that energy transfer across the pool occurs more by convection. The cryogenic liquid problem goes beyond the scope of this work, however a new approach based on Raleigh Benard convection theory will be demonstrated here to show its effect on our case.

B.1 Natural Convection Model in Enclosures

According to this theory, the fluid is enclosed between two boundaries maintained at different temperatures. Actually when the components of the pool evaporate the same amount is replaced to the surface as a result of natural convection. Natural convection flow patterns in rectangular enclosures with low height to length ratios (aspect ratio) have been experimentally determined. Cormack et al have studied the phenomena of buoyancy driven convection in shallow lakes as a shallow cavity problem (Cormack et al. 1974). In most of these shallow cavity problems formation of unsteady cells have been observed which they attribute to turbulence (Klosse and Ullersma 1973) also did some work with a gas in two-dimensional low aspect ratio rectangular enclosures with two vertical walls at different uniform temperature and a corresponding linear temperature gradient along the horizontal walls. In both these it has generally been observed that in low aspect ratio enclosures the flow over most of the length is parallel counter flow with fluid in the upper half of the cavity flowing from warm end to cold end.

For our case, the chemical spilled is enclosed in rectangular or cylindrical enclosures and the aspect ratio is usually in the range of 10^{-3} or less than that. In these cases steady convection begins in the form of two-dimensional rolls and as time progresses the vertical boundaries will have a stabilizing effect due to additional viscous shear that dampens thermal instabilities.

In this Raleigh Benard mechanism, the free convection may be actually opposed by viscous forces and may therefore occur only if the temperature difference for vertical boundaries is greater than some critical value. The parameter used to check the criticality is called the Raleigh number expressed as follows (Byron et al. 2000):

$$Ra = Gr.Pr = \rho^2 . g . (T_g - T_{pool}) . h^3 . c_p . \beta / \mu . k$$

where,

Gr= Grashof Number

Pr = Prandtl number

T_g =Temperature of the ground.

β= Thermal expansion coefficient

μ =Dynamic viscosity of the solution.

For Raleigh numbers below the critical value of 1101, the fluid is stationary and conduction is the mode of heat transfer through the static fluid, otherwise convection cells exists inside the pool. In this new approach the three dimensional Navier Stokes equation needs to be solved to obtain the mass flux from the pool.

B.1.2 Basic Equations

The equations of mass, momentum and heat transfer can be derived from the Navier-Stokes equation and these can be represented as follows:

$$\nabla . \vec{u} = 0$$

$$\frac{\partial u}{\partial t} + \frac{u_x . \partial u_x}{\partial x} + \frac{u_y . \partial u_{xy}}{\partial y} + \frac{u_z . \partial u_z}{\partial z} = -\nabla . P + \Pr . Ra . T_{pool} + \Pr . \nabla^2 u$$

$$\frac{\partial T_{pool}}{\partial t} + \frac{u_x . \partial T_{pool}}{\partial x} + \frac{u_y . \partial T_{pool}}{\partial y} + \frac{u_z . \partial T_{pool}}{\partial z} = \nabla^2 T_{pool}$$

In the above equations,

u = Velocity of the fluid

T_{pool}= Temperature of the pool.

x, y, z = The respective rectangular coordinates.

$u_{x,,}\ u_{y,} u_z$ =velocity components in the x,y,z direction.

The problem can be solved with many modified assumptions compared to the improved surface evaporation model. The pool can be divided into fine meshes using GAMBIT as shown below. The structured grid (Figure 34) can then be used in fluent after setting the necessary boundary conditions.

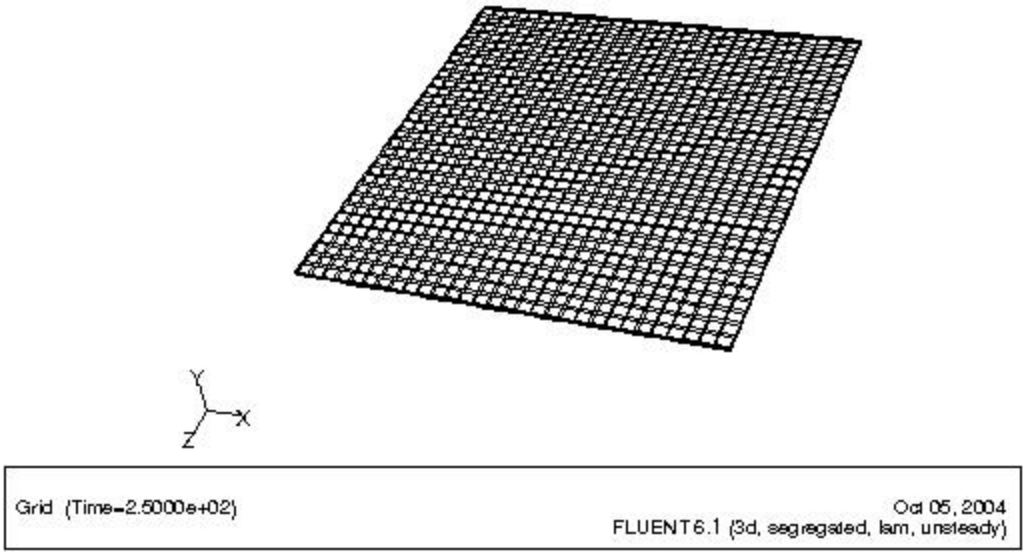

Fig. 334. Meshed pool surface

B.1.3 Boundary Condition and Test Conditions

The ground temperature is assumed to be varying and the dike temperature is assumed to be equal to the ambient temperature. The ground surface is set at a higher temperature compared to the ground temperature. And an initial heat flux was also specified for the groundside. The whole system was solved for energy and momentum balance with an initial kick off velocity of 0.001 m/sec. The program was run for 250 seconds to check if there is any significant temperature gradient along the horizontal section of the pool. The results are presented as follows for two different runs.

B.1.4 Run 1

The following picture (Figure 35) shows the temperature variation across the top surface and clearly shows that there is some temperature gradient initially under the set conditions.

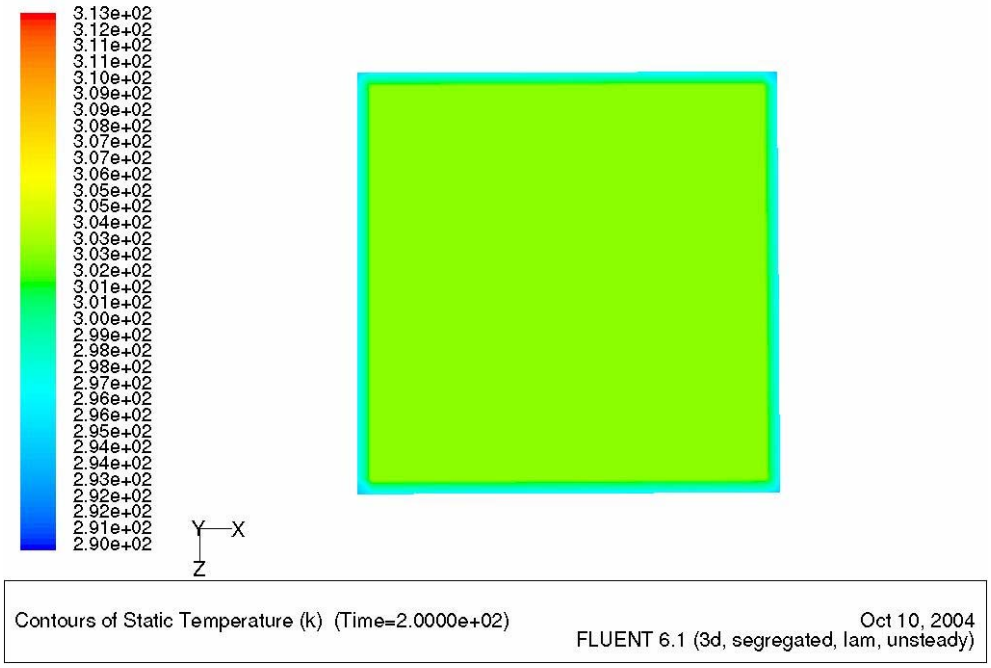

Fig. 35. Top surface contour for a 10 cm pool depth

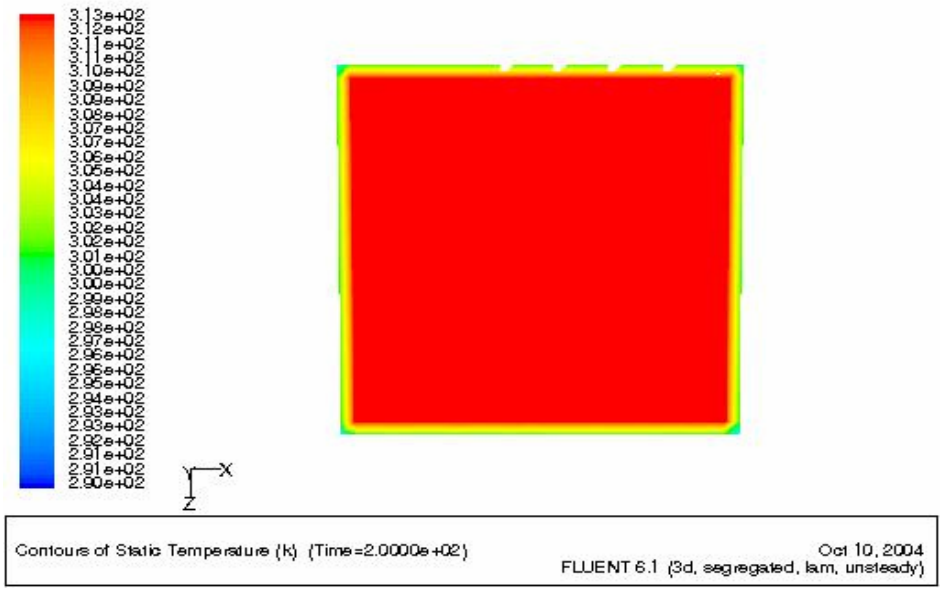

Fig. 346. Ground surface contour for a 10 cm pool depth

This picture again (Figure 36) shows that there is not any significant temperature gradient across the surface in the bottom section of the pool.

B.1.5 Run 2

In this run the conditions were modified slightly by increasing the heat flux and decreasing the thickness of the liquid pool. The result for the bottom surface clearly shows that the Benard cells are starting to appear. This indicates that there could be some small changes in temperature at the bottom with time.

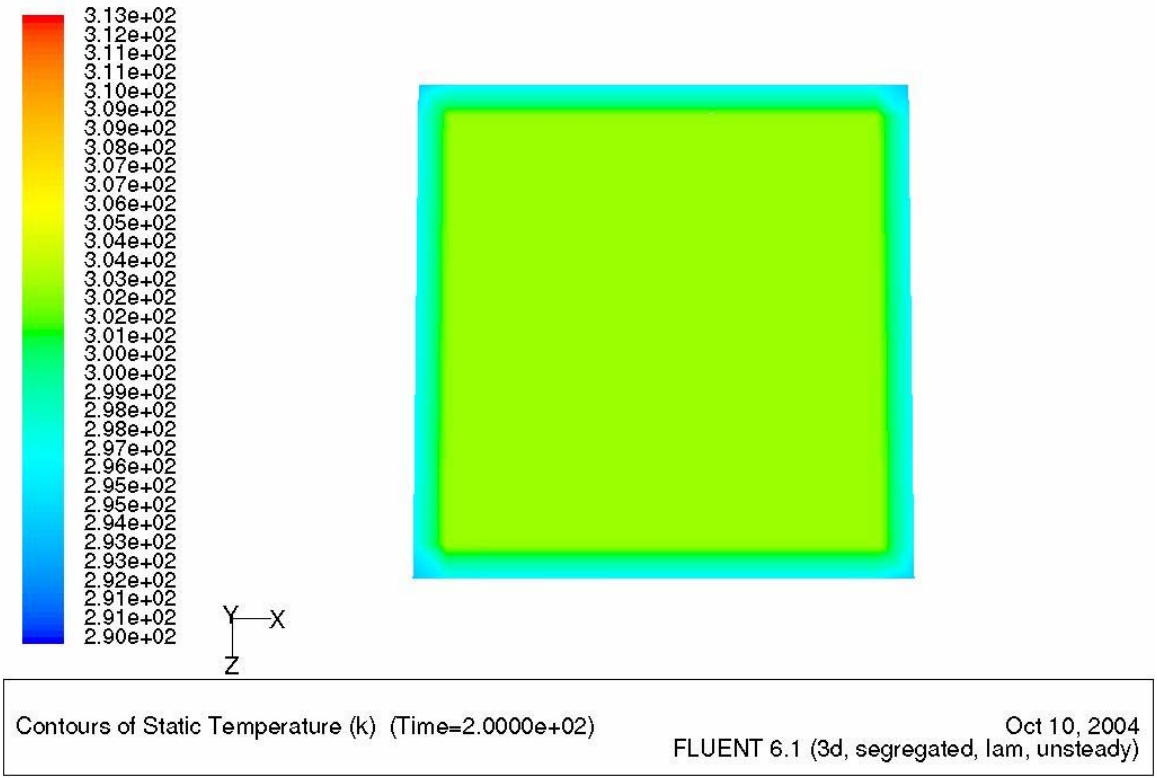

Fig. 37. Top surface contour for a 5 cm pool depth

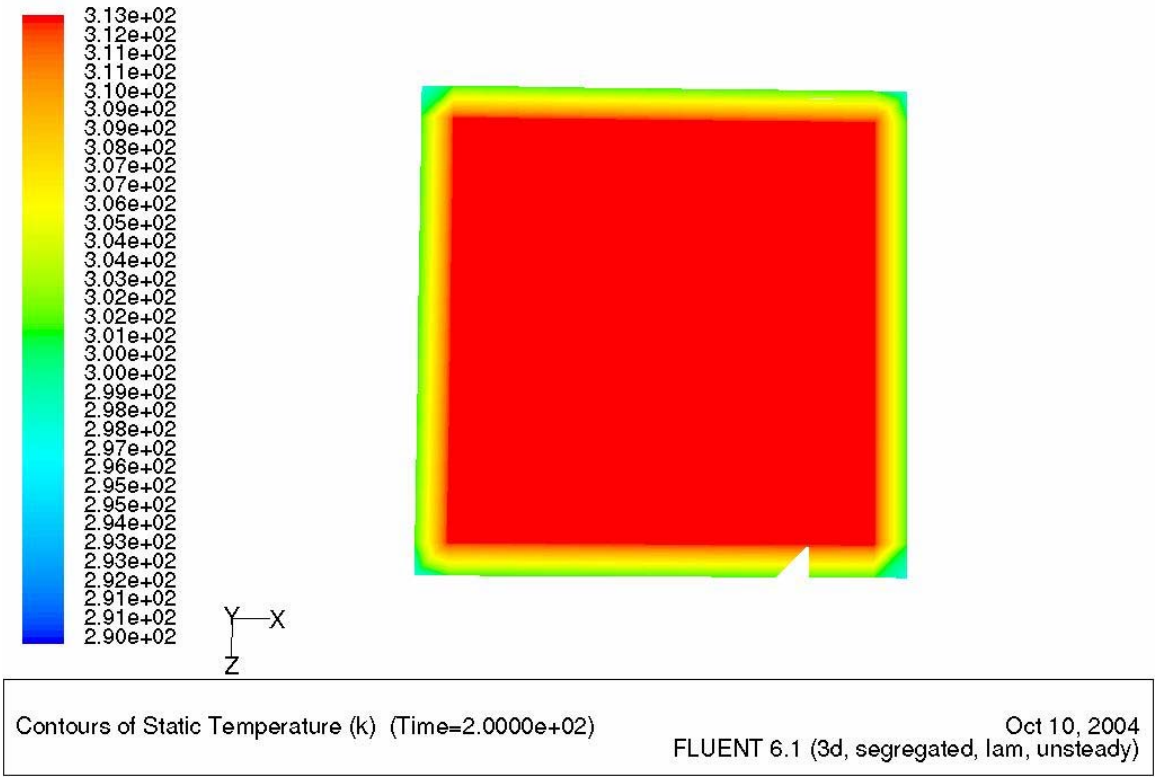

Fig. 38. Ground surface contour for a 5 cm pool depth

Hence for the first case (Figure 37) there is no vigorous mixing and hence the temperature difference across the pool can be assumed to be constant. But the second case (Figure 38) needs to be tested for more time instants .A separate routine needs to be written and attached to FLUENT with a specified profile for each of these properties and this will make the system more dynamic. This new system can then be tested for other chemicals mostly cryogenics and the 3-d model can be used to estimate the source at every point inside the pool. This in turn will be a very realistic input for the Computational Fluid Dynamic models.

APPENDIX C

CASE STUDY FOR DILUTE PROCESS STREAMS

The different water solution streams solvent water, stripper overheads, deep well flow and rich water comprise of many hazardous chemicals in extremely low concentrations. The spills of such dilute contaminated solutions might result in a liquid pool with some volatile/toxic components. The objective of this study was to identify the best practices used in the industry to deal with low concentration chemical spills and check the applicability of these models to such chemical spills.

The various models that were studied as a part of the literature survey are the following.

- ESL evaporative Model
- Army Model
- Shell Model
- AWS Model
- CHEMMAP
- LSM-90/LPOOL

The LPOOL model theory was found to be the most suitable one to the problem and hence the model was reprogrammed in Matlab with some simplified assumptions. The Matlab program was then linked to an excel file which is very simple to handle. The whole package is very interactive and the program is also very robust, as it has been tested with a variety of streams.

C.1 Nomographs

A set of nomographs were also developed which could be used by a process engineer to read off the amount chemical that could have escaped from a given quantity of spill. A few sample nomographs for some of the process streams are given as follows.

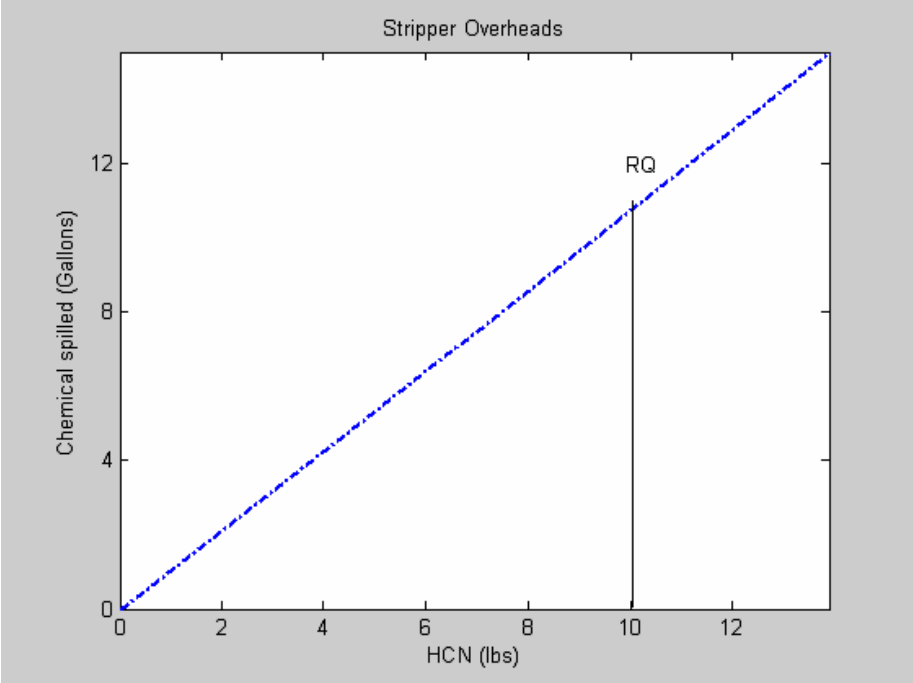

Fig. 39. Quantity of HCN released into air

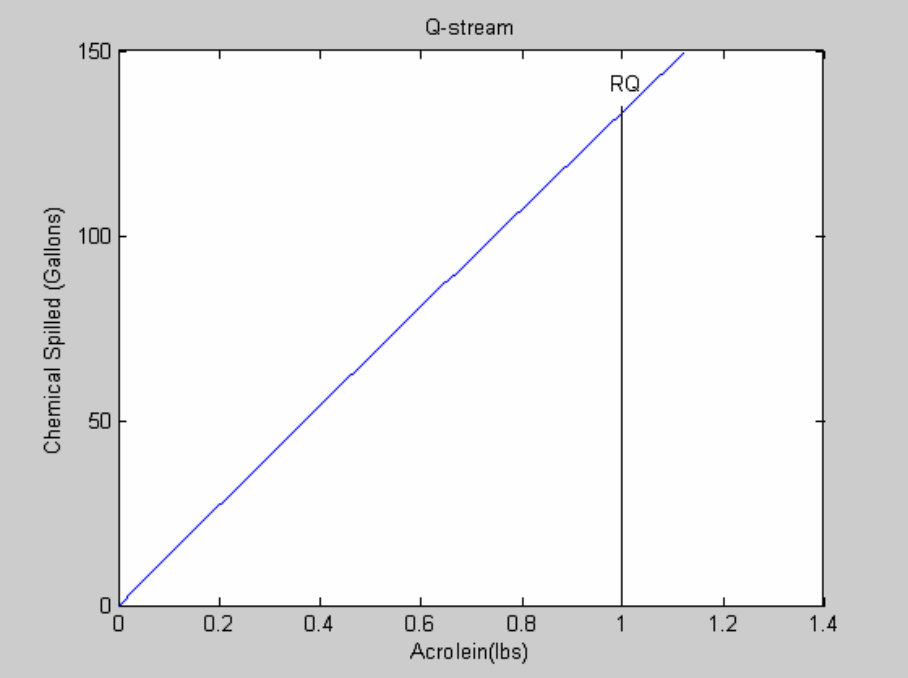

Fig. 40. Quantity of acrolein released into air

In the above graphs (Figures 39 and 40) the Y-axis represents the quantity of spill in gallons and the X-axis represents the amount of chemical released into air. These graphs can be used to check if the released chemical has exceeded the reportable quantity. These nomographs could be used directly for a known spill quantity or if the conditions vary the model can be rerun and a new set of graphs can be prepared.

VITA

Vijay Raghunathan was born to Mr.Raghunathan and Mrs. Rama Raghunathan on March 3, 1981. Vijay completed his schooling at P.S.Senior Secondary School, Chennai in the year 1998. He pursued his career in chemical engineering at University of Madras and earned his B.Tech degree in May 2002. Later Vijay entered Texas A&M University in the year 2002 to obtain his master's degree in chemical engineering. Vijay Raghunathan's permanent address is:

A-5, Lakshmi Enclave,
Apt # 16, First Street Abhirampuram,
Chennai, 600018